GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[X] ORIGINAL [ ] REVISION NO. ____

Project No. G-41-671 (Q5359-0A0) GTRC/GIT DATE 7 / 5 / 85

Project Director: A. Erbil School/Lab Physics

Sponsor: Alfred P. Sloan Foundation

650 Fifth Ave. NY NY 10111

Type Agreement: Grant BR-2512

Award Period: From 9/16/85 To 9/15/88 (Performance) 9/15/87 (Reports)

Sponsor Amount:	This Change	Total to Date
Estimated:	$	$
Funded:	$ 25,000	$ 25,000

Cost Sharing Amount: $ N/A Cost Sharing No: N/A

Title: Alfred P. Sloan Foundation Award to Dr. Ahmet E. Erbil School of Physics

ADMINISTRATIVE DATA OCA Contact Ralph Grede x4820

1) Sponsor Technical Contact:

Mr. Eric Wanner
Alfred P. Sloan Foundation
630 Fifth Avenue
New York NY 10111
212/ 582-0450

2) Sponsor Admin/Contractual Matters:

Mr. Eric Wanner
Alfred P. Sloan Foundation
630 Fifth Avenue
New York, NY 10111
202/582-0450

Defense Priority Rating: N/A Military Security Classification: N/A

(or) Company/Industrial Proprietary: N/A

RESTRICTIONS

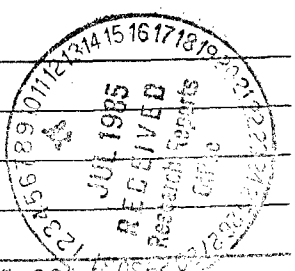
See Attached N/A Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with Georgia Tech - However no equipment is proposed

COMMENTS:

The maximum indirect rate allowable under this grant is 15%.



SPONSOR'S I. D. NO. 02.500.015.85.002

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NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 04/30/90

Project No. G-41-671 Center No. Q5339-0A0

Project Director ERBIL A School/Lab PHYSICS

Sponsor ALFRED P SLOAN FOUNDATION/

Contract/Grant No. BR-2512 Contract Entity GTRC

Prime Contract No.

Title ALFRED P. SLOAN RESEARCH FELLOWSHIPS

Effective Completion Date 900330 (Performance) 900531 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	N	
Final Report of Inventions and/or Subcontracts	N	
Government Property Inventory & Related Certificate	N	
Classified Material Certificate	N	
Release and Assignment	N	
Other	N	

Comments

Subproject Under Main Project No.

Continues Project No.

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Other	N
	N

PROGRESS REPORT

Grant: Alfred P. Sloan Research Fellowship

Period Covered: 9/16/1985 - 9/15/1986

Project Director: Dr. Ahmet Erbil, Physics, Georgia Tech

Last year was a busy and exciting year for us. Most of the time was spent in setting up the facilities for the growth and characterization of metal-semi-conductor superlattices. A sophisticated commercial MOCVD system (Cambridge Instruments, MR102, cost $300,000) was bought and installed. The final test on this system will be completed at the end of this month. Thereafter this commercial system will be ready for the growth of metal-semiconductor superlattices. In addition to the commercial system, we have designed and built a simple MOCVD system to study the pyrolysis of various metalorganic compounds.

In the past year, we had a major breakthrough in the preparation of the organometallic compounds of lanthanum. We demonstrated that the alkyl substituted tricyclopentadienyl lanthanum compounds are highly volitale and stable, making it suitable for MOCVD deposition. Currently, we are in the process of scaling up the reaction to have enough compounds to grow LaTe/PbTe superlattices. One feature of our synthesis method is that it can easily be extended to the preparation of other rare earth and transition metal compounds. An old superconducting magnet obtained from the School of Physics is being refurbished to carry out the optical and the electrical transport measurements on metal-semiconductor superlattices.

GEORGIA TECH 1885-1985

DESIGNING TOMORROW TODAY

Georgia Institute of Technology
Grants and Contracts Accounting Dept.
Lyman Hall/Emerson Building
Atlanta, Georgia 30332-0259
Telephone: (404) 894-4624; 2629

December 4, 1986

Mr. Eric Wanner
Alfred P. Sloan Foundation
630 Fifth Avenue
New York, NY 10111

RE: Grant No. BR-2512

Dear Mr. Wanner:

We have enclosed a copy of the Georgia Institute of Technology's Project Budget and Expenditure Report for the period beginning September 16, 1985 and ending September 15, 1986.

If you require additional information, please contact me at 404-894-5522.

Sincerely,

Kelley Rogers
Accountant II

kar

Enclosure

xc: A. Erbil
F. Gleason

ALFRED P SLOAN FOUNDATION - BR 2512
BUDGET & EXPENDITURES REPORT
SEPTEMBER 16,1985 - SEPTEMBER 15, 1986
G-41-671/243Q5339-0A0

	PERSONAL SERVICES	FRINGE BENEFITS	OVERHEAD	TOTAL
BUDGET	$17,936.58	$3,802.55	$3,260.87	$25,000.00
EXPENDITURES				
1985				$0.00
SEPT. 16-30				$0.00
OCTOBER				$0.00
NOVEMBER	$3,322.22	$697.67	$602.98	$4,622.87
DECEMBER	$1,661.11	$348.83	$301.49	$2,311.43
1986				$0.00
JANUARY				$0.00
FEBRUARY				$0.00
MARCH				$0.00
APRIL				$0.00
MAY				$0.00
JUNE				$0.00
JULY	$112.50		$16.88	$129.38
AUGUST				$0.00
SEPT. 1-15				$0.00
TOTAL FY86 EXPENDITURES	$5,095.83	$1,046.50	$921.35	$7,063.68
FREE BALANCE	$12,840.75	$2,756.05	$2,339.52	$17,936.32

Alfred P. Sloan Research Fellowship

Annual Progress Report

September 16, 1986 - September 15, 1987

Principal Investigator:

Ahmet Erbil

School of Physics

Georgia Institute of Technology

Atlanta, GA 30332

Tel.: (404) 894-6817

Table of Contents

Synopsis of Progress During the Grant Period 9/16/86 - 9/15/87

1.1 Study of Artificially Layered Materials

1.1.1 Thin Film Growth

Currently the major growth technique utilized is the metalorganic chemical vapor deposition (MOCVD) technique. This technique has the capability to grow thin films with atomic level control to fabricate hetero-structures and superlattices. The MOCVD technique is also very suitable to the large scale production of electronic and photonic thin films. In addition, we are currently building a metalorganic molecular beam epitaxy (MO-MBE) system. This technique combines the best features of MOCVD and MBE techniques. We have two MOCVD systems operational. The first one is a commercial MOCVD system (Cambridge Instruments, MR102) with 5 MO source lines and 2 hydride lines, suitable for the deposition of a single layer, hetero-structure and supperlatices. The second MOCVD system is homemade and suitable for the deposition of simple layered structures and study of the mechanisms of MOCVD.

1.1.2 CVD Precursor Development

The availability of the suitable precurcors are essential for successful deposition of the films by the CVD technique. This component of the program focuses on the creation of novel metalorganic compounds suitable for the deposition of rare earth metals, particularly for the deposition of La and LaTe by MOCVD. We have had major breakthroughs in this area in the past year.

I believe that this puts us in a unique position in the world in the deposition of all of the rare earth metals. These precursors will have applications in the metallization of microcircuitry, in the deposition of protective coatings, newly discovered Cu based oxide superconductors and solar cells, etc.

1.1.3 Study of Thin Films Grown by MOCVD

In this area, our purpose was to understand the growth conditions and their relationship to the properties of the thin films obtained. Even though the immediate goal was to establish a data base for the growth of LaTe/PbTe superlattices on CdTe buffer layers grown on GaAs, the work has much broader applications in microelectronics and optoelectronics. Among the major achievements in this area are: detailed understanding of the growth mechanism of MOCVD, successful deposition of high quality PbTe films by MOCVD, and first successful deposition of La and LaTe films by MOCVD. The films grown have been characterized for their chemical, structural, electrical and optical properties. The results will be submitted soon for publications in the form of several papers.

In the study of the MOCVD growth mechanism, we have grown CdTe films on GaAs (111) wafers systematically to relate the growth rate and the surface morphology to the growth conditions. It is important to understand the growth of CdTe layers, because such layers will be used as the buffer layers for the growth of LaTe/PbTe superlattices. By using a mass transport model through the boundary layer and the gas-solid interface, we have calculated the growth rate as a function of temperature for a broad range, including the mass input limited regime, the diffusion limited regime and the surface kinetic limited

regime. We have obtained excellent agreement between the theory and the experiments. Currently, we are extending our understanding of MOCVD from CdTe to the growth of other compounds such as PbTe, LaTe and LaPe/PbTe. This work has been carried out in collaboration with P. Anderson of Texas Instruments.

We have grown epitaxial layers of PbTe on either GaAs wafers or on CdTe buffer layers grown on GaAs wafers. PbTe grows epitaxially with the [100] direction on GaAs (100) and [100] direction on GaAs (111). Tetraethylead and diisopropyltelluride were used as the MOCVD precursors for low temperature deposition (temperature range 320-450 C). The PbTe films were n or p type depending on the growth conditions. The IR transmission measurements have indicated a sharp absorption at the band-gap energy. We used both Hall effect and IR reflectivity measurements to determine the carrier concentration and mobilities. The mobility for MOCVD grown PbTe films was smaller than the bulk value. This may be a result of microcracks in the film due to thermal expansion mismatch. In support of this idea is the observation of microcracks in most of the PbTe films grown under the optical microscope.

We have deposited La and LaTe thin films in the homemade MOCVD system by using the precurcors discovered at Georgia Tech. The suitable deposition temperature range was 550-650 C. These studies were preliminary in nature and were aimed at understanding the decomposition kinetics of the new precursors. Quartz plates were used as substrates. We utilized both argon and hydrogen as the carrier gas. Electron microprobe analysis exhibited up to 10% carbon incorporation in La films grown with Ar carrier gas. We expect great reduction in carbon incorporation in films grown with hydrogen carrier gas. We are in the process of analyzing these films. Also we have observed much less carbon incorporation in LaTe films.

We have utilized various on or off-campus facilities to carry out the

characterization of thin films. Double crystal x-ray diffraction experiments were done by P. Huang and S. Stock of Materials Engineering, the electron microprobe analysis by G. Freeman of Georgia Tech Research Institute, and IR reflectivity measurements by S. Perkovitz of Emory University. We have also utilized the Hall effect system in A. Rohatgi's laboratory in Electrical Engineering.

1.2 Study of Naturally Layered Oxide Superconductors

Right after the announcement of the breakthrough on the copper-oxide-based high T_c superconductors, we initiated a program on these materials. Even though this effort was initially started by using the funds from a Sloan Research Fellowship and an IBM Faculty Development award, there have been clear overlaps with our DOE contract starting in the summer of 1987.

Our initial work in this area involved the synthesis and characterization of $Y_1Ba_2Cu_3O_7$ compounds in the usual manner. By optimizing the heat treatment and making substitution, we were able to obtain superconductors on a routine basis with transition temperatures above 90 K. Starting in July of 1987, our focus shifted to the discovery of superconductivity at even higher temperatures.

After a careful systematic study, we were led to several compositions exhibiting evidence of superconductivity at room temperature and above. The highest observed onset temperature is 550 K. This work is described in detail in a paper accepted by Phys. Rev. B. A copy of this paper is provided in the attachment.

Alfred P. Sloan Research Fellowship

Annual Progress Report

September 16, 1987 - September 15, 1988

Principal Investigator:

Ahmet Erbil

School of Physics

Georgia Institute of Technology

Atlanta, GA 30332

Tel.: (404) 894-6817

TABLE OF CONTENTS

1. Introduction:

In this report, we provide a summary of the progress made during the grant period (September 16, 1987 - September 15, 1988). Initially the focus of this program was on the development of underlying science and technology for the fabrication of metal-semiconductor superlattices. The major motivation for this work was to search for excitonic superconductivity in these structures as predicted by theory, in addition to the obvious microelectronic applications. After the discovery of superconductivity with transition temperatures above 77K, naturally we have turned our attention also to this new class of materials.

We describe briefly below our work carried under this program on the development of metal-semiconductor superlattices (artificially layered materials) and on the copper oxide based superconductors (naturally layered materials).

2. Study of Artificially Layered Materials

2.1 Thin Film Growth

Currently the major growth technique utilized is the metalorganic chemical vapor deposition (MOCVD) technique. This technique has the capability to grow thin films with atomic level control to fabricate heterostructures and superlattices. The MOCVD technique is also very suitable to the large scale production of electronic and photonic thin films. In addition, we are currently building a metalorganic molecular beam epitaxy (MO-MBE) system. This technique combines the best features of MOCVD and MBE techniques. We have three MOCVD systems operational. The first one is a commercial MOCVD system (Cambridge Instruments, MR102) with 5 MO source lines and 2 hydride lines, suitable for the deposition of a single layer, hetero-structure and superlattices. The other two MOCVD systems are homemade and

suitable for the deposition of oxide thin films.

2.2 CVD Precursor Development

The availability of the suitable precursors are essential for successful deposition of the films by the CVD technique. This component of the program focuses on the creation of novel metalorganic compounds suitable for the deposition of rare earth metals, particularly for the deposition of La and LaTe by MOCVD. We have had major breakthroughs in this area in the past few years. I believe that this puts us in a unique position in the world in the deposition of all of the rare earth metals. These precursors will have applications in the metallization of microcircuitry, in the deposition of protective coatings, newly discovered Cu based oxide superconductors and solar cells, etc. A patent disclosure has been filed to cover these inventions.

2.3 Study of Non-Oxide Thin Films Grown by MOCVD

In this area, our purpose was to understand the growth conditions and their relationship to the properties of the thin films obtained. Even though the immediate goal was to establish a data base for the growth of LaTe/PbTe superlattices on CdTe buffer layers grown on GaAs, the work has much broader applications in microelectronics and optoelectronics. Among the major achievements in this area are: detailed understanding of the growth mechanism of MOCVD, successful deposition of high quality PbTe films by MOCVD, and first successful deposition of La and LaTe films by MOCVD. The films grown have been characterized for their chemical, structural, electrical and optical properties. The results will be submitted soon for publication in the form of several papers.

In the study of the MOCVD growth mechanism, we have grown CdTe films on GaAs (111) wafers systematically to relate the growth rate and the surface

morphology to the growth conditions. It is important to understand the growth of CdTe layers, because such layers will be used as the buffer layers for the growth of LaTe/PbTe superlattices. By using a mass transport model through the boundary layer and the gas-solid interface, we have calculated the growth rate as a function of temperature for a broad range, including the mass input limited regime, the diffusion limited regime and the surface kinetic limited regime. We have obtained excellent agreement between the theory and the experiments, as discussed in the preprint attached. Currently, we are extending our understanding of MOCVD from CdTe to growth of other compounds such as PbTe, LaTe and LaTe/PbTe. This work has been carried out in collaboration with P. Anderson of Texas Instruments.

We have grown epitaxial layers of PbTe on either GaAs wafers or on CdTe buffer layers grown on GaAs wafers. PbTe grows epitaxially with the [111] direction on GaAs(100) and [100] direction on GaAs(111). Tetraethylead and diisopropyltelluride were used as the MOCVD precursors for low temperature deposition (temperature range 320-450 C). The PbTe films were n- or p-type depending on the growth conditions. The IR transmission measurements have indicated a sharp absorption at the band-gap energy. We used both Hall effect and IR reflectivity measurements to determine the carrier concentration and mobilities. The mobility for MOCVD grown PbTe films was smaller than the bulk value. This may be a result of microcracks in the film due to thermal expansion mismatch. In support of this idea is the observation of microcracks in most of the PbTe films grown under the optical microscope.

We have deposited La and LaTe thin films in the homemade MOCVD system by using the precursors discovered at Georgia Tech. The suitable deposition temperature range was 550-650 C. These studies were preliminary in nature and were aimed at understanding the decomposition kinetics of the new precursors. Quartz plates were used as substrates. We utilized both argon and hydrogen as

the carrier gas. Electron microprobe analysis exhibited up to 10% carbon incorporation in La films grown with Ar carrier gas. We expect great reduction in carbon incorporation in films grown with hydrogen carrier gas. We are in the process of analyzing these films. Also we have observed much less carbon incorporation in LaTe films.

Epitaxial thin films of bismuth telluride, Bi_2Te_3 have been successfully deposited first time on GaAs(111) by MOCVD. Bi_2Te thin films were metallic and can be used to deposit metal-semiconductor superlattices. Also, Bi_2Te_3 is a thermoelectric material and may be used to fabricate monolithic micro-refrigerators to cool semiconductor or superconductor devices. High quality epitaxial films of Bi_2Te were obtained on GaAs(111) substrates at $320^{o}C$ as evidenced by optical microscopy, x-ray diffraction and ion channeling. Film properties, such as mobility and carrier concentration were studied in the temperature range 80-300K. The films were of p-type with a carrier concentration of 2×10^{20} $1/cm^3$ at room temperature.

We have utilized various on or off-campus facilities to carry out the characterization of thin films. Double crystal x-ray diffraction experiments were carried out in collaboration with P. Huang and S. Stock of Materials Engineering, the electron microprobe analysis by G. Freeman of Georgia Tech Research Institute, and IR reflectivity measurements by S. Perkovitz of Emory University. We have also utilized the Hall effect system in A. Rohatgi's laboratory in Electrical Engineering.

We feel that we have acquired large enough data base for the growth of metal-semiconductor superlattices to search for excitonic superconductivity. However, we would like to continue this line of research at a slower pace and concentrate on the naturally layered oxide superconductors in the next three years because we can make an immediate impact in this area. Therefore last month, we submitted a renewal three year proposal to DOE for the study of

MOCVD and MOMBE grown high-T_c superconducting films.

3. Study of Naturally Layered Oxide Superconductors

3.1 Oxide Bulk Material Studies:

Right after the announcement of the breakthrough on the copper-oxide-based high T_c superconductors, we initiated a program on these materials. Even though this effort was initially started by using the funds from a Sloan Research Fellowship and an IBM Faculty Development award, there have been clear overlaps with our DOE contract starting in the summer of 1987.

Our initial work in this area involved the synthesis and characterization of $Y_1Ba_2Cu_3O_7$ compounds in the usual manner. By optimizing the heat treatment and making substitution, we were able to obtain superconductors on a routine basis with transition temperatures above 90 K. Starting in July of 1987, our focus shifted to the discovery of superconductivity at even higher temperatures. After a careful systematic study, we were led to several compositions exhibiting evidence of possible superconductivity at room temperature or above. The highest observed onset temperature is 550 K. This work is described in detail in a paper submitted to Physical Review B. The fraction of the superconducting phase seems to be very small (1 part in 10^4) and to make further progress in this area we need more sensitive instruments.

3.2 Oxide Thin Film Studies:

Our research effort in this area focuses on the development of the MOCVD technique to provide high quality superconducting thin films on large area substrates for fundamental studies and device applications. Our results show that after post annealing, C-axis oriented $YBa_2Cu_3O_{7-x}$ superconducting films can be obtained reproducably with a transition onset temperature at 93K and a zero resistance temperature at 84K on yttria-stabilized zirconia (100) (YSZ)

substrates. We have already submitted a paper to Appl. Phys. Lett. (a copy is provided in the attachment) and we will present an invited paper in November on the subject. These initial results show that the MOCVD technique can be used for the deposition of high quality superconducting thin films. MOCVD is currently the dominant technique in the deposition of large area device quality III-V and II-VI compounds in the production mode.

The use of superconducting coatings and thin films is severaly limited at this point because of the lack of suitable substrates. The most widely used substrates are MgO(100), YSZ and $SrTiO_3$. However, these substrates are very expensive and not available with large areas. To address this problem we have started depositing these materials by MOCVD on common substrates, such as glass plates, silicon and sapphire. The MgO film deposited on a glass plate had very smooth surface morphology and was optical quality. It had also almost one hundred percent texturing with (100) direction perpendicular to the substrate surface. This is surprising in view of the fact that glass substrate is amorphous and MgO has a cubic structure. Next we would like to deposit superconducting thin films on these (100) oriented MgO buffer layers deposited on glass plates. It is well known that single crystal MgO (100) substrates give high quality superconducting films with very high critical currents ($T_c \sim 10^6$ A/cm^2). Therefore the growth of oriented MgO films on common cheap substrates as buffer layers may have profound implications for the large scale utilization of the superconducting thin films and coatings.

4. Publications Under This Grant

1. "Evidence for Possible Stable Superconductivity at 500K", A. Erbil, A. C. Wright and E. P. Boyd, Phys. Rev. B37, 555 (1988).

2. "C-Axis Oriented $YBa_2Cu_3O_{7-x}$ Superconducting Films by Metalorganic Chemical Vapor Deposition", K. Zhang, B. S. Kwak, E. P. Boyd, A. C. Wright and A. Erbil (accepted by Appl. Phys. Lett.).

3. "Growth Mechanism of CdTe Films by Organometallic Vapor Phase Epitaxy", A. Erbil, A. C. Wright and P. L. Anderson (to be submitted to J. Crystal Growth).

4. "OMVPE Growth and Properties of PbTe Films on GaAs", A. Erbil and K. T. Pollard (to be submitted to Appl. Phys. Lett.).

5. "Ion Channeling Studies of the MOCVD Grown CdTe Films on GaAs", B. Wilkens, K. T. Pollard and A. Erbil (to be submitted to Appl. Phys. Lett.).

6. "Organometallic Vapor Phase Epitaxy of Bi_2Te_3 on GaAs(111)", A. Erbil, K. T. Pollard and B. Wilkens (to be submitted to Appl. Phys. Lett.).

5. Meetings and Symposia Under the Grant

A) Invited

1. "Possible Very High T_c Superconductors", A. Erbil, Panel Discussion, Materials Research Society Meeting, April 5-8, 1988, Reno, Nevada.

2. "C-Axis Oriented $YBa_2Cu_3O_{7-x}$ Superconducting Films by Metalorganic Chemical Vapor Deposition", A. Erbil, K. Zhang, B. S. Kwak, E. P. Boyd, and A. C. Wright, Conference on the Science and Technology of Thin Film Superconductors, November 14-18, 1988, Colorado Springs, Colorado.

B) Contributed

1. "MOCVD Growth Mechanism of II-VI Compounds", Bull. Am. Phys. Soc. 32, 530 (1987).

2. "MOCVD of II-VI Compounds", Epicon '87, November 16-20, 1987, South Africa.

3. "Evidence for Possible Stable Superconductivity at 500K", Symp. High T_c Superconductors, Mateials Research Society, Nov. 30 - Dec. 3 (1987), Boston, MA.

4. "Study of MOCVD Grown PbTe Films", Bull. Am. Phys. Soc. 33, 246 (1988).

5. "Ion Channeling Studies of the MOCVD Grown CdTe Films on GaAs", B. Wilkens and A. Erbil, Materials Research Society Meeting, Boston, MA, Nov. 28 - Dec. 3, 1988.

Accepted by
Phys. Rev. B

Evidence for Possible Stable Superconductivity at 500 K

A. Erbil, A. C. Wright, and E. P. Boyd*

School of Physics

Georgia Institute of Technology

Atlanta, GA 30332

Abstract

A stable and reproducible resistive transition with onset at about 550 K has been observed in a new Y-Ba-Cu-O compound system and attributed to a transition to a possible superconducting state. The possibility of superconductivity has been verified by the observation of i) a dc Josephson-like effect up to 390 K which is quenched in a high external magnetic field and ii) a marked reduction in the onset temperature with increasing bias current density. Both observations are consistent with granular superconductivity.

PACS numbers: 74.10.+v, 74.50.+r, 74.70.Ya

The discovery of superconductivity in lanthanum barium copper oxide by Bednorz and Muller[1] at 30 K, followed by the discovery of superconductivity at 93 K in yttrium barium copper oxide by Wu et al.[2] has created great excitement in the scientific community as well as in the popular press in the past year. To date, the reliable and reproducible T_c for zero resistance is about 95 K. Higher T_c's such as 160 K[3] and 240 K[4] have been reported in the system $YBa_2Cu_3O_{7-\delta}$. But, in all of these reports, reproducibility of the observation is lacking. In this Letter, we report the observation of a stable state consistent with superconductivity well above room temperature in a new Y-Ba-Cu-O compound system. We specifically report detailed results on samples with nominal starting compositions $Y_1Ba_7Cu_1O_x$ and $Y_6Ba_6Cu_1O_x$. These samples show resistive transitions with onsets at about 550 K and a dc Josephson-like effect up to 390 K which is quenched in an external magnetic field.

The samples were prepared from the appropriate mixtures of Y_2O_3, $BaCO_3$, CuO and BaF_2 powders through solid-state reaction. Well mixed starting components were pulverized in a high-purity alumina crucible prior to firing in a platinum tray between 900-930 C for 2h in air. The firing and pulverizing were repeated two times to improve homogeneity. The powders were cold pressed into pellets (of 10 mm diameter and 1 mm thickness) and sintered either in air or under flowing oxygen gas at 950 C up to 113 h. The furnace then was cooled to room temperature at about 10 C/min.

The dc resistivity measurements were made using the conventional four-point probe technique after platinum wires were attached to the samples with silver epoxy. Magnetic fields for the Josephson effect measurements up to 7.1 T were generated by a fixed field superconducting magnet. Preliminary magnetization measurements were made by using a vibrating sample magnetometer.

We have prepared three different classes of samples which show evidence

of possible superconductivity above 200 K. Class I, II and III samples had nominal starting compositions of $Y_1Ba_2Cu_3O_5F_2$, $Y_1Ba_7Cu_1O_x$ and $Y_6Ba_6Cu_1O_x$, respectively. We were led to Class II and Class III compositions through an iterative process by identifying the stoichiometry of phases in previous samples by using an electron microprobe and then trying to generate each phase separately by appropriate composition of starting materials. The first sample made in Class I had very high resistivity and exhibited a broad current density dependent transition with onset at 260 K. However, subsequent attempts to reproduce this broad transition all failed. Even though we utilized the same starting compositions and processing conditions as the first sample, these subsequent samples exhibited very low resistivities with sharp superconducting transition at 90 K, without any indication of a transition at higher temperatures. The first sample preserved its transition after sitting unprotected on the shelf for four months and provided a starting point for our discovery of other compounds with even higher transition temperatures. Electron microprobe analysis indicated the existence of at least five different types of grains in this sample. Among the samples prepared with the observed grain compositions only those with the nominal composition $Y_1Ba_7Cu_1O_x$ (Class II) exhibited possible superconductivity at room temperature and above. Class II samples were highly resistive at high temperature but exhibited possible granular type superconductivity. In all the samples prepared in Class II we observed the dc Josephson-like effect. The onset for the transition in Class II samples was around 500 K. The electron microprobe analysis of a Class II sample exhibited large areas with nominal composition $Y_6Ba_6Cu_1O_x$ and an overall composition of $Y_2Ba_3Cu_1O_x$. The samples prepared with the starting nominal composition $Y_6Ba_6Cu_1O_x$ (Class III) were less resistive and had transition temperatures around 500 K. We therefore believe that in both

Class II and Class III samples, possible superconductivity takes place in the same phase. The electron microprobe analysis of a Class III sample yielded an overall composition of $Y_{4.1}Ba_{2.5}Cu_1O_x$ and showed the existence of four different phases including $Y_2Ba_1Cu_1O_x$, $Y_3Ba_3Cu_6O_x$, $Y_1Ba_2Cu_3O_x$ and $Y_9Ba_5Cu_1O_x$. The latter phase constitutes about 60 percent of the sample.

It is not clear at this point why the overall composition of the samples after sintering is so much different than the starting compositions in Class II and Class III samples. Both Class II and Class III samples were very moisture-sensitive and required special protection, particularly for the measurements above room temperature. In all of the samples which exhibited high-T_c transitions we observed an increase in T_c with thermal cycling. The transition temperature stabilizes after a few cycles. In this Letter, we report detailed results only for Class II and Class III samples.

The temperature dependence of the resistance of a Class III sample for different bias currents is shown in Fig. 1. This measurement was made in a furnace with a temperature range of 300-573 K. Each resistance curve is scaled to its value at 573 K to elucidate the bias current effect on the transition. The resistivity was about 60 KΩ-cm at 573 K for 700nA bias current and decreased at least three orders of magnitude to about 60 Ω-cm upon cooling to room temperature. Even though this is still a very high resistivity, it is consistent with the existence of a thermally smeared Josephson junction as will be discussed below. A possible explanation in terms of a semiconductor-to-metal transition in one of the phases in our sample is ruled out by the bias current dependence of the resistivity, and our Josephson-like effect studies discussed below. At a bias current of 10 nA, the onset appears at 550 K even though a sharp increase in resistivity above 562 K may be indicative of yet another transition at a higher temperature.

The onset of possible superconductivity has been taken as the resistivity peak as in some earlier studies.[5] This assumption appears to be valid in percolative systems, i.e., when different crystalline phases with interpenetrating grains are present as found in our compounds.

The 10, 50 and 90 percent drops in resistivity take place at 522 K, 476 K and 424 K for 10 nA bias current, respectively. As would be expected from a granular superconductor,[6] higher current densities reduce T_c appreciably. Just above the transition, there is an increase in resistivity with decreasing temperature at high bias currents. This behavior was also observed in the original Ba-La-Cu-O system[1] and is associated with the beginning of localization.

Fig. 2 shows the voltage-current characteristic at room temperature for a Class II sample for different values of external magnetic field. At zero field we clearly see finite current at "zero" voltage - this is reminiscence of a dc Josephson effect (of course, thermal smearing of the weak link network response prevents exactly zero voltage at finite current). The critical current I_c is about 18 nA at room temperature. The possibility of the existence of a true dc Josephson effect is reinforced by the magnetic field dependence of the current-voltage curve, i.e., the critical current is strongly reduced by high magnetic fields, even though normal resistivity of the junction changes very little. If we assume that the voltage-current characteristic in Fig. 2 represents a dc Josephson effect then the normal state resistance R_n measured at a voltage of 260 mV is 8.17 MΩ. The I_cR_n product is about 147 mV. Assuming that the voltage-current characteristic is determined by the Josephson junction with the highest critical current,[7] the theory of Ambegaokar et al.[8] permits one to estimate the value of the energy gap Δ from the I_cR_n product. We obtain $\Delta = 94 \pm 10$ meV at room temperature.

From the estimated critical temperature of 476 K (midpoint of the resistive transition), the value of the energy gap $\Delta(0)$ yields $2\Delta(0)/k_BT_c = 5 \pm 1$. This result is larger than would be expected from a weak-coupling BCS prediction of $2\Delta/k_BT_c = 3.5$, but is consistent with strongly coupled superconductors.

The strong temperature dependence of the possible Josephson effect for a Class II sample is shown in Fig. 3. There is a pronounced "rounding" in the I-V characteristics with increasing temperature. This observation is well-known and reflects the effect of thermal fluctuations on dc Josephson current.[9] The nonlinear possible Josephson behavior of the I-V characteristics almost disappears at 390 K. It is interesting to note that the possible Josephson critical current at 340 K is higher than that at 295 K and the normal resistance R_n is lower. But the product I_cR_n at 340 K is smaller than that at 295 K and more rounded - consistent with the theory.[9]

For Josephson junctions, the length of the weak link must be less than several times the coherence length of the material.[10] Since the coherence length in the copper oxide based superconductors is considered to be several nanometers,[11] we suggest that the observed possible Josephson junctions in our samples occur at grain boundaries[12,13] or twin boundaries.[14] This idea is further supported by our observation that the Josephson-like effect has been observed more often in our more structurally disordered Class II samples.

We have performed a preliminary magnetization measurement on one Class III sample to estimate the volume fraction of possible superconducting phase. The measurement exhibited a complex behavior, showing diamagnetism at room temperature and paramagnetism at 100 K. This observation suggests that, in our multiphase samples, the diamagnetic contribution is superimposed on a paramagnetic contribution and that the latter becomes dominant at low temperature. If we attribute all of the diamagnetism measured to super-

conductivity then the superconducting volume fraction would be about 0.03 percent.

Evidently if we are observing superconductivity, the superconducting regions occupy a very small fraction of the total volume yet produce drastic changes in the electrical behavior. We discount the possibility of surface layer superconductivity, because measurements made on internal surfaces exposed after fracture yielded similar results. We propose that grain boundaries contain the possible superconducting regions; a grain boundary network can provide three dimensional electrical connectivity yet remain a very small fraction of the total volume. Nevertheless, it is not clear at this point whether the observed possible superconductivity is intrinsic to the grain boundaries arising from the mixed phases, or if it is a result of a certain phase which happens to form at the grain boundaries. In any event, it appears that high yttrium and barium content is required for the observation of this novel phenomenon.[15]

It may be argued that the observed effect is related to the positive temperature coefficient resistance (PTCR) effect.[16] The PTCR effect is observed in ferroelectric materials and, in fact, it is directly related to a ferroelectric transition. First of all, there is no known evidence that there is a ferroelectric transition in the Y-Ba-Cu-O system. Even if there was a ferroelectric transition in our samples, we can eliminate the PTCR effect as a possible explanation for our measurements by studying the I-V characteristics and the bias current effect on the R-T curves. In the PTCR effect, I is proportional to V at low voltages and to V^2 at high voltages.[16] In addition, the PTCR effect predicts an increase in the transition temperature with increasing bias current. These characteristics for the PTCR effect are qualitatively inconsistent with our measurements shown in Fig. 1 and Fig. 2.

We can also eliminate as possible explanations other known phenomena such as thermopower effect, battery formation, thermal heating, various rectifing junction effects, etc., by contrasting the I-V curves and their magnetic dependences. At this point, only the superconductivity phenomenon seems to be consistent with all of our observations.

In conclusion, a stable and reproducible resistive transition with onset at about 550 K has been observed in a new Y-Ba-Cu-O compound system. The possibility of superconductivity has been verified by the observation of current-voltage characteristics reminiscent of a dc Josephson effect up to 390 K. The onset temperature is markedly reduced by high current densities, consistent with granular superconductivity. Even though all of the observations we have are consistent with superconductivity, we can not eliminate the existence of an unknown effect as the cause at this point. Work continues both to measure the Meissner effect and to identify the high-T_c phases.

We wish to thank A. Zangwill, E. W. Thomas, R. A. Young and R. J. Higgins for helpful discussions and encouragement, G. Freeman and J. Johnson for the electron microprobe analysis, T. H. Huang for the use of his high field magnet, and L. Swatzendruber and R. Shull for the magnetization measurements. We acknowledge financial support from Alfred P. Sloan Foundation, IBM, Research Corporation, and the Department of Energy under Grant No. DE-FG05-86ER45266.

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15. If the very high-T_c phase do indeed contain high Ba and Y content, it is plausible that they further increase the separation between Cu-O planes as compared to the $Y_1Ba_2Cu_3O_x$ compound.

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Figures

Fig. 1. The temperature dependence of the resistance of a Class III sample for various bias currents. The subsequent heating cycles were carried out in the order 2, 3 and 1.

Fig. 2. The current-voltage characteristics at room temperature for a Class II sample in various magnetic fields. The intermediate value of the magnetic field was unknown and obtained by placing the sample off-center in the magnet.

Fig. 3. The current-voltage characteristics in zero magnetic field for a Class II sample at various temperatures.

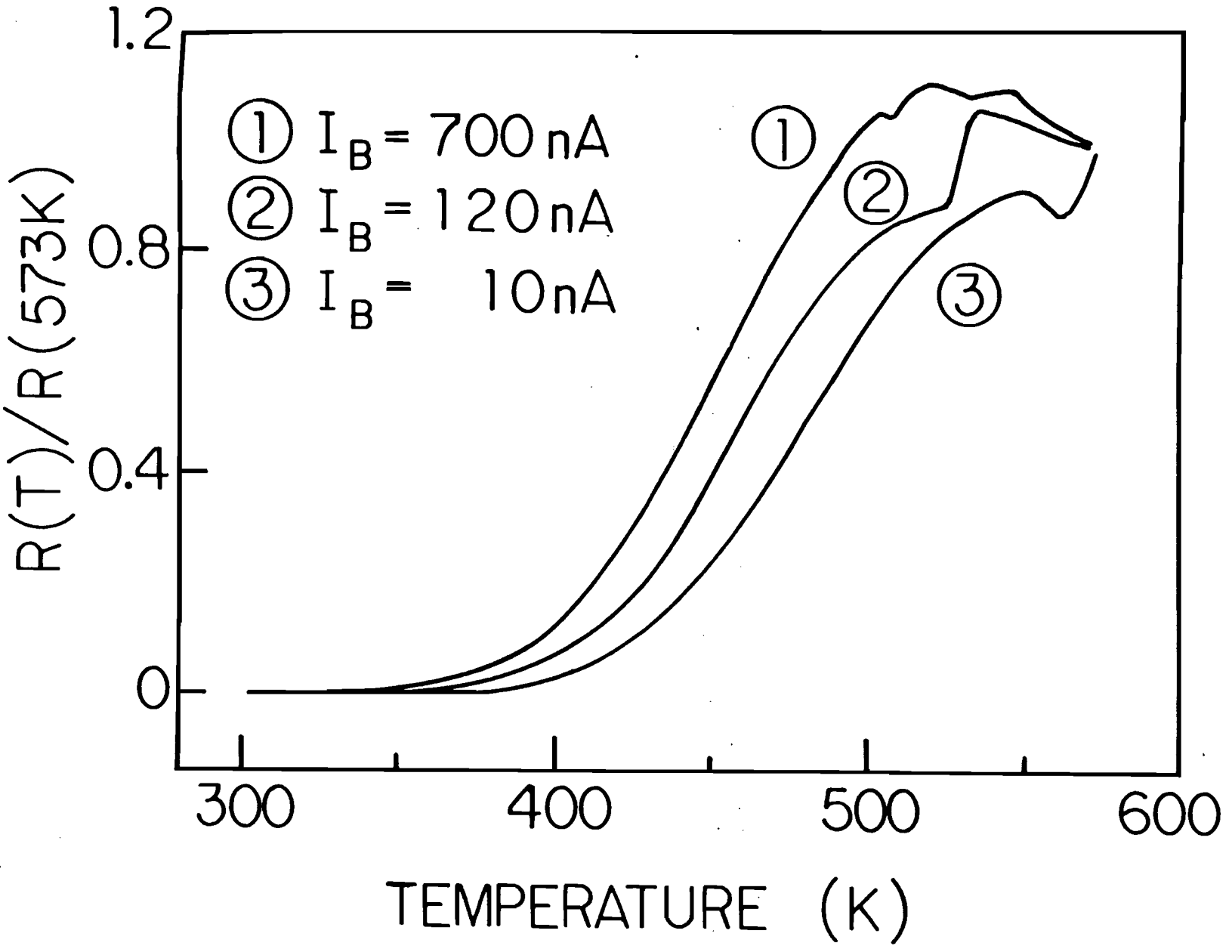
1.2
0.8
0.4
0
R(T)/R(573K)
① I_B = 700 nA
② I_B = 120 nA
③ I_B = 10 nA
①
②
③
300
400
500
600
TEMPERATURE (K)

FIG. 1

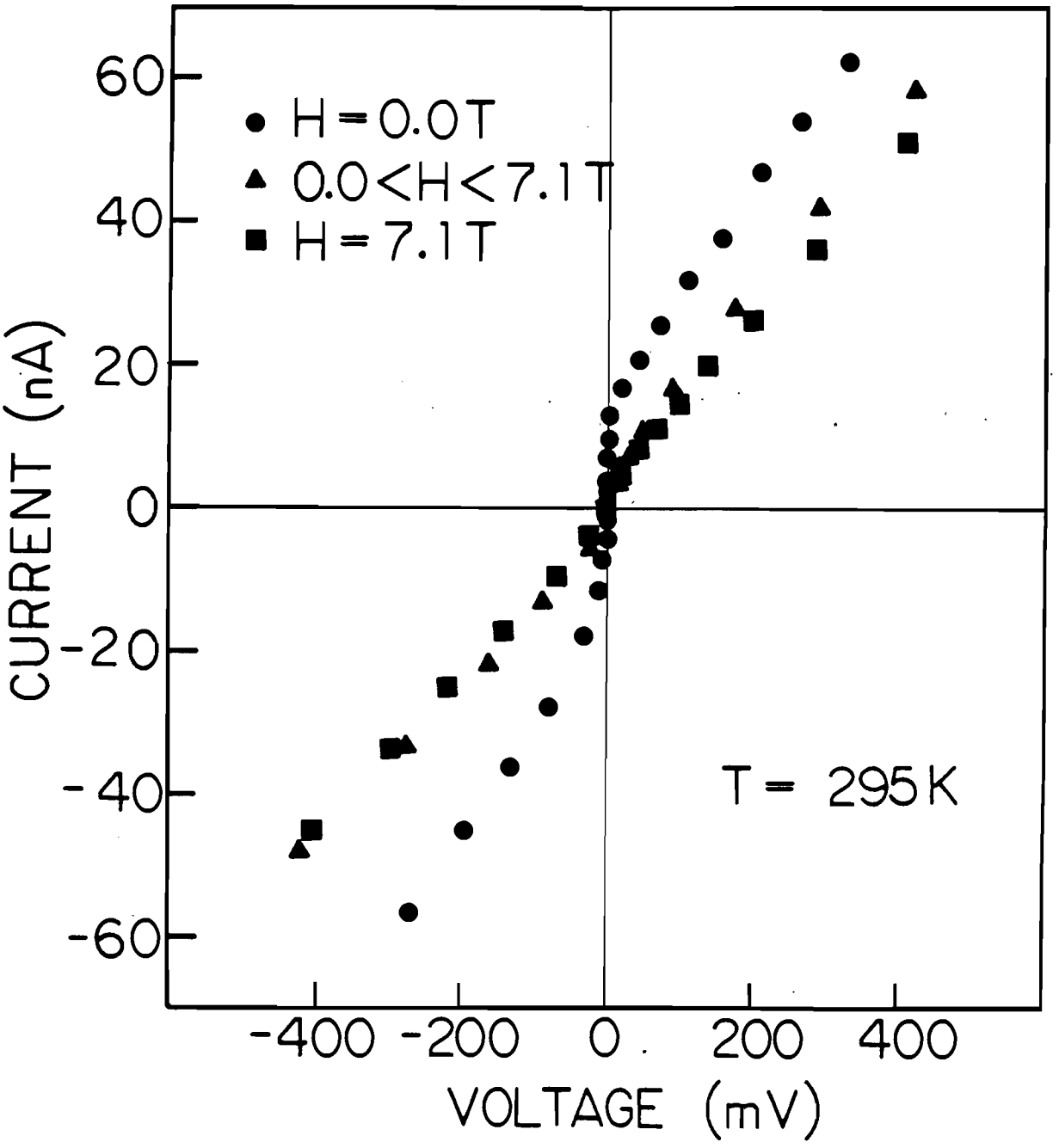
60
40
20
0
-20
-40
-60
CURRENT (nA)
H = 0.0T
0.0 < H < 7.1T
H = 7.1T
T = 295K
-400
-200
0
200
400
VOLTAGE (mV)

FIG. 2

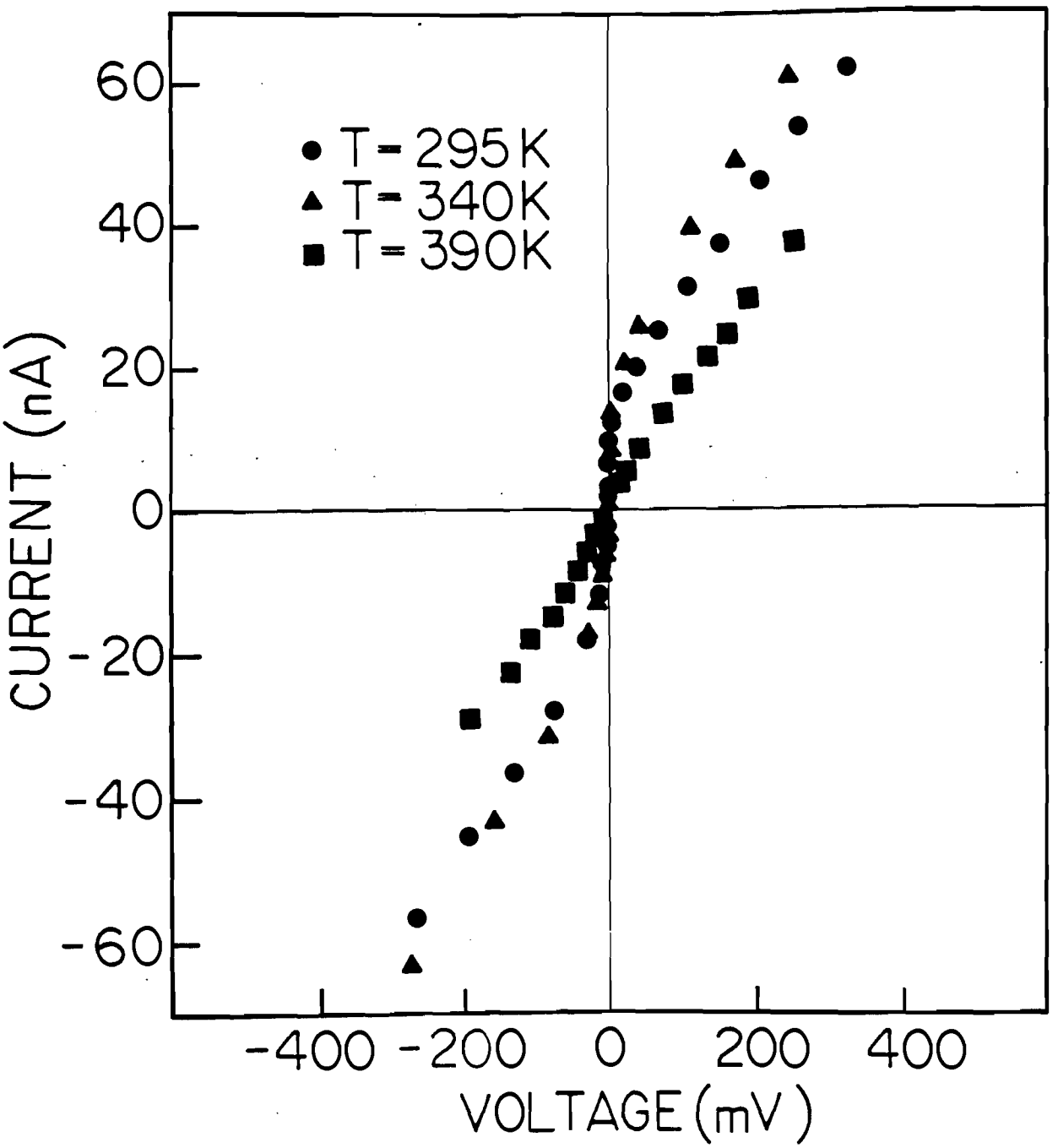
60
40
20
0
-20
-40
-60
CURRENT (nA)
● T = 295K
▲ T = 340K
■ T = 390K
-400
-200
0
200
400
VOLTAGE (mV)

FIG. 3

Alfred P. Sloan Research Felloship

Final Report

September 16, 1985 - September 15, 1989

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TABLE OF CONTENTS

STUDY OF HIGH T_c SUPERCONDUCTING THIN FILMS GROWN BY MOCVD

1. Introduction:

In this report, we provide a final summary of the progress made during the grant period (September 16, 1985 - September 16, 1989). Initially the focus of this program was on the development of underlying science and technology for the fabrication of metal-semiconductor superlattices. The major motivation for this work was to search for excitonic superconductivity in these structures as predicted by theory, in addition to the obvious microelectronic applications. After the discovery of superconductivity with transition temperatures above 77K, naturally we have turned our attention also to this new class of materials.

We describe briefly below our work carried under this program on the development of techniques to grow metal-semiconductor superlattices (artificially layered materials) and on the copper oxide based superconductors (naturally layered materials).

2. Study of Artificially Layered Materials

2.1 Thin Film Growth

Currently the major growth technique utilized is the metalorganic chemical vapor deposition (MOCVD) technique. This technique has the capability to grow thin films with atomic level control to fabricate heterostructures and superlattices. The MOCVD technique is also very suitable to the large scale production of electronic and photonic thin films. We have three MOCVD systems operational. The first one is a commercial MOCVD system (Cambridge Instruments, MR102) with 5 MO source lines and 2 hydride lines, suitable for the deposition of a single layer, heterostructure and superlattices. The other two MOCVD systems are homemade and suitable for the

deposition of oxide thin films.

2.2 CVD Precursor Development

The availability of the suitable precursors are essential for successful deposition of the films by the CVD technique. This component of the program focuses on the creation of novel metalorganic compounds suitable for the deposition of rare earth metals, particularly for the deposition of La and LaTe by MOCVD. We have had major breakthroughs in this area in the past three years. I believe that this puts us in a unique position in the world in the deposition of all of the rare earth metals. These precursors will have applications in the metallization of microcircuitry, in the deposition of protective coatings, newly discovered Cu based oxide superconductors and solar cells, etc.

2.3 Study of Non-Oxide Thin Films Grown by MOCVD

In this area, our purpose was to understand the growth conditions and their relationship to the properties of the thin films obtained. Even though the immediate goal was to establish a data base for the growth of LaTe/PbTe superlattices on CdTe buffer layers grown on GaAs, the work has much broader applications in microelectronics and optoelectronics. Among the major achievements in this area are: detailed understanding of the growth mechanism of MOCVD, successful deposition of high quality PbTe films by MOCVD, and first successful deposition of La and LaTe films by MOCVD. The films grown have been characterized for their chemical, structural, electrical and optical properties. The results will be submitted soon for publication in the form of several papers, despite delay due to higher priority given to oxide thin films.

In the study of the MOCVD growth mechanism, we have grown CdTe films on

GaAs (111) wafers systematically to relate the growth rate and the surface morphology to the growth conditions. It is important to understand the growth of CdTe layers, because such layers will be used as the buffer layers for the growth of LaTe/PbTe superlattices. By using a mass transport model through the boundary layer and the gas-solid interface, we have calculated the growth rate as a function of temperature for a broad range, including the mass input limited regime, the diffusion limited regime and the surface kinetic limited regime. We have obtained excellent agreement between the theory and the experiments, as discussed in the preprint attached. On the theoretical side, we have interacted very closely with Prof. Zangwill in the School of Physics at Georgia Tech. Currently, we are extending our understanding of MOCVD from CdTe to growth of other compounds such as PbTe, LaTe and LaTe/PbTe. This work has been carried out in collaboration with P. Anderson of Texas Instruments.

The [111] CdTe/[111] GaAs heterostructure system has been studied in detail by means of MeV ion channeling. It is found that the epitaxy is quite good (backscatter minimum yields of 15%) for thickness greater than 100 Å, which is remarkable considering the 14% lattice mismatch between film and substrate. We have shown that the mismatch results in defects in the interface region in addition to strain produced by epitaxial growth. It has been observed that there is a disturbance in the Cd sublattics as evidenced by displaced Cd atoms protruding into the [211] channels in an asymmetric manner causing an apparent offset in the Cd angular yield minimum. A model was proposed based on Te vacancy density of 1.7% as a possible explanation for the Cd behavior. This work has been in collaboration with B. Wilkens at Bellcore.

We have grown epitaxial layers of PbTe on either GaAs wafers or on CdTe buffer layers grown on GaAs wafers. PbTe grows epitaxially with the [111] direction on GaAs(100) and [100] direction on GaAs(111). Tetraethylead and diisopropyltelluride were used as the MOCVD precursors for low temperature deposition (temperature range 320-450 C). The PbTe films were n- or p-type

depending on the growth conditions. The IR transmission measurements have indicated a sharp absorption at the band-gap energy. We used both Hall effect and IR reflectivity measurements to determine the carrier concentration and mobilities. The mobility for MOCVD grown PbTe films was smaller than the bulk value. This may be a result of microcracks in the film due to thermal expansion mismatch. In support of this idea is the observation of microcracks in most of the PbTe films grown under the optical microscope.

We have deposited La and LaTe thin films in the homemade MOCVD system by using the precursors discovered at Georgia Tech. The suitable deposition temperature range was 550-650 C. These studies were preliminary in nature and were aimed at understanding the decomposition kinetics of the new precursors. Quartz plates were used as substrates. We utilized both argon and hydrogen as the carrier gas. Electron microprobe analysis exhibited up to 10% carbon incorporation in La films grown with Ar carrier gas. We expect great reduction in carbon incorporation in films grown with hydrogen carrier gas. We are in the process of analyzing these films. Also we have observed much less carbon incorporation in LaTe films.

Epitaxial thin films of bismuth telluride, Bi_2Te_3 have been successfully deposited first time on GaAs(111) by MOCVD. Bi_2Te_3 thin films were metallic and can be used to deposit metal-semiconductor superlattices. Also, Bi_2Te_3 is a thermoelectric material and may be used to fabricate monolithic micro-refrigerators to cool semiconductor or superconductor devices. High quality epitaxial films of Bi_2Te_3 were obtained on GaAs(111) substrates at $320^{o}C$ as evidenced by optical microscopy, x-ray diffraction and ion channeling. Film properties, such as mobility and carrier concentration were studied in the temperature range 80-300K. The films were of p-type with a carrier concentration of 2×10^{20} cm^{-3} at room temperature.

We have utilized various on or off-campus facilities to carry out the characterization of thin films. Double crystal x-ray diffraction experiments

were carried out in collaboration with P. Huang and S. Stock of Materials Engineering, the electron microprobe analysis by G. Freeman of Georgia Tech Research Institute, and IR reflectivity measurements by S. Perkovitz of Emory University. We have also utilized the Hall effect system in A. Rohatgi's laboratory in Electrical Engineering.

We feel that we have acquired large enough data base for the growth of metal-semiconductor superlattices to search for excitonic superconductivity. However, we would like to continue this line of research at a slower pace and concentrate on the artificially layered oxide compounds in the near future, because we can make an immediate impact in this area.

3. Study of Naturally Layered Oxide Superconductors

3.1 Oxide Bulk Material Studies:

Right after the announcement of the breakthrough on the copper-oxide-based high T_c superconductors, we initiated a program on these materials. Even though this effort was initially started by using the funds from a Sloan Research Fellowship and an IBM Faculty Development award, there have been clear overlaps with our DOE contract starting in the summer of 1987.

Our initial work in this area involved the synthesis and characterization of $Y_1Ba_2Cu_3O_7$ compounds in the usual manner. By optimizing the heat treatment and making substitution, we were able to obtain superconductors on a routine basis with transition temperatures above 90 K. Starting in July of 1987, our focus shifted to the discovery of superconductivity at even higher temperatures. After a careful systematic study, we were led to several compositions exhibiting evidence of possible superconductivity at room temperature or above. The highest observed onset temperature is 550 K. This work is described in detail in a paper submitted to Physical Review B. The fraction of the superconducting phase seems to be very small (1 part in 10^4).

3.2 Oxide Thin Film Studies:

Our research effort in this area in the past two years has focused on the development of the MOCVD technique to provide high quality superconducting thin films on large area substrates for fundamental studies and device applications. We have successfully deposited thin films of $Y_1Ba_2Cu_3O_{7-x}$ and $Tl_2CaBa_2Cu_2O_y$ by MOCVD with high quality. The results have been reported in the form of several papers and invited talks. The papers are provided in the attachment. Our results show that after post annealing, C-axis oriented $YBa_2Cu_3O_{7-x}$ superconducting films can be obtained reproducably with a transition onset temperature at 93K and a zero-resistance temperature at 84K on yttria-stabilized zirconia (100) (YSZ) substrates. Superconducting $Tl_2CaBa_2Cu_2O_y$ thin films have been grown on single crystal sapphire $(1\bar{1}02)$ substrate without a buffer layer. Superconducting transition temperatures with onset above 100K and zero-resistance at 94K has been obtained with heat treatment at 500°C in oxygen.

The use of superconducting coatings and thin films is severaly limited at this point because of the lack of suitable substrates. The most widely used substrates are MgO(100), YSZ and $SrTiO_3$. However, these substrates are very expensive and not available with large areas. To address this problem we have started depositing these materials by MOCVD on common substrates, such as glass plates, silicon and sapphire. The MgO film deposited on a glass plate had very smooth surface morphology and was optical quality. It had also almost one hundred percent texturing with (100) direction perpendicular to the substrate surface. The detailed results are provided in a paper provided in the attachment. This is surprising in view of the fact that glass substrate is amorphous and MgO has a cubic structure. Next we would like to deposit superconducting thin films on these (100) oriented MgO buffer layers deposited on glass plates. It is well known that single crystal MgO (100) substrates

give high quality superconducting films with very high critical currents (T_c ~ 10^6 A/cm^2). Therefore the growth of oriented MgO films on common cheap substrates as buffer layers may have profound implications for the large scale utilization of the superconducting thin films and coatings.

4. Publications Under This Grant

1. "Evidence for Possible Stable Superconductivity at 500K", A. Erbil, A. C. Wright and E. P. Boyd, Phys. Rev. B37, 555 (1988).

2. "Metalorganic Chemical Vapor Deposition of Highly Textured Superconducting $YBa_2Cu_3O_{7-x}$ Films", K. Zhang, B. S. Kwak, E. P. Boyd, A. C. Wright and A. Erbil, in "Science and Technology of Thin Film Superconductors", ed. by R. D. McConnell and S. A. Wolf (Plenum, New York, 1989), p. 271.

3. "C-Axis Oriented $YBa_2Cu_3O_{7-x}$ Superconducting Films by Metalorganic Chemical Vapor Deposition", K. Zhang, B. S. Kwak, E. P. Boyd, A. C. Wright and A. Erbil, Appl. Phys. Lett. 54, 380 (1989).

4. "Metalorganic Chemical Vapor Deposition of [100] Textured MgO Thin Films", B. S. Kwak, E. P. Boyd, K. Zhang, A. Erbil, and B. Wilkens, Appl. Phys. Lett. 54, 2542 (1989).

5. "Metalorganic Chemical Vapor Deposition of $Tl_2CaBa_2Cu_2O_y$ Superconducting Thin Films on Sapphire", K. Zhang, E. P. Boyd, B. S. Kwak, A. C. Wright, and A. Erbil, Appl. Phys. Lett. 55, 1258 (1989).

Accepted for Publication

1. "MeV Ion Channeling Studies of [111] CdTe Films on [111] GaAs Substrates", B. Wilkens, K. Pollard and A. Erbil (J. Appl. Phys.).

In Preparation

1. "Growth Mechanism of CdTe Films by Organometallic Vapor Phase Epitaxy", A. Erbil and P. L. Anderson (for Appl. Phys. Lett.).

2. "OMVPE Growth and Properties of PbTe Films on GaAs", A. Erbil and K. T. Pollard (for Appl. Phys. Lett.).

3. "Organometallic Vapor Phase Epitaxy of Bi_2Te_3 on GaAs (111)", A. Erbil, K. T. Pollard and B. Wilkens (for J. Electronic Mat.).

5. Meetings and Symposia Under This Grant

A) Invited

1. A. Erbil, "Possible Very High T_c Superconductors", Panel discussion, Materials Research Society Meeting, April 5-8, 1988, Reno, Nevada.

2. A. Erbil, K. Zhang, B. S. Kwak, E. P. Boyd and A. C. Wright, "C-Axis Oriented $YBa_2Cu_3O_{7-x}$ Superconducting Films by Metalorganic Chemical Vapor Deposition", Conference on the Science and Technology of Thin Film Superconductors, November 14-18, 1988, Colorado Springs, Colorado.

3. A. Erbil, K. Zhang, B. S. Kwak and E. P. Boyd, "A Review of Metalorganic Chemical Vapor Deposition of High-Temperature Superconducting Thin Films", SPIE's 1989 Symposium, Oct. 8-13, 1989, Santa Clara, CA.

B) Contributed

1. A. Erbil and P. L. Anderson, "MOCVD Growth Mechanisms of II-VI Compounds", Bull. Am. Phys. Soc. 32, 530 (1987).

2. P. L. Anderson and A. Erbil, "MOCVD of II-VI Compounds", Epicon '87, November 16-20, 1987, South Africa.

3. A. Erbil, A. C. Wright and E. P. Boyd, "Evidence for Possible Stable Superconductivcity at 500 K", Symp. High T_c Superconductors, Materials Research Society, Nov. 30-Dec. 3 (1987), Boston, MA.

4. A. Erbil and K. T. Pollard, "Study of MOCVD Grown PbTe Films", Bull. Am. Phys. Soc. 33, 246 (1988).

5. B. Wilkens and A. Erbil, "Ion Channeling Studies of the MOCVD Grown CdTe Films on GaAs", Materials Research Society Meeting, Boston, MA, Nov. 28 - Dec. 3, 1988.

6. A. Erbil, K. Zhang, B. S. Kwak, E. P. Boyd and A. C. Wright, "C-Axis Oriented $YBa_2Cu_3O_{7-x}$ Superconducting Films by Metalorganic Chemical Vapor Deposition", Conference on the Science and Technology of Thin Film Superconductors, November 14-18, 1988, Colorado Springs, Colorado.

7. K. Zhang, B. S. Kwak, E. P. Boyd, A. C. Wright, and A. Erbil, "Effects of Substrate and Post-Annealing Conditions on Metalorganic Chemical Vapor Deposition of $YBa_2Cu_3O_{7-x}$ Thin Films", Bull. Am. Phys. Soc. 34, 603 (1989).

8. A. Erbil, K. Pollard and B. Wilkens, "Study of Bi_2Te_3 Thin Films Grown by MOCVD", Bull. Am. Phys. Soc. 34, 937 (1989).

9. B. S. Kwak, E. P. Boyd, K. Zhang, and A. Erbil, "Growth of Highly Textured MgO Thin Films by MOCVD", Bull. Am. Phys. Soc. 34, 937 (1989).

c-axis oriented $YBa_2Cu_3O_{7-x}$ superconducting films by metalorganic chemical vapor deposition

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Highly textured single phase superconducting $YBa_2Cu_3O_{7-x}$ films have been successfully grown on the yttria-stabilized zirconia (100) substrates by using the metalorganic chemical vapor deposition technique. The as-deposited films grown at 650 °C were homogeneous mixtures of the related metal oxides and carbonates. Subsequent thermal annealing under oxygen flow yielded single phase superconducting films whose thickness corresponded to the deposition rates of approximately 10 μm/h. After the post-annealing the films deposited on the yttria-stabilized zirconia substrates exhibited a highly textured x-ray pattern with *c* axis perpendicular to the substrate surface. These films show an onset superconducting transition temperature of 93 K with the resistance becoming zero at 84 K.

The recent discovery of some oxide superconducting materials with transition temperatures above 77 K represents a major breakthrough for both science and technology.[1,2] But before these materials fulfill their promise, processing techniques need to be developed to prepare these materials with high quality in the required forms and sizes. High T_c superconducting thin films with zero resistance transitions above liquid-nitrogen temperatures have been prepared by various techniques, including coevaporation of the metallic constituents from individual sources,[3–6] pulsed laser deposition,[7] sputtering,[8,9] molecular beam deposition,[10] the sol-gel method,[11] and multilayer evaporation.[12] Our research effort focuses on the development of the metalorganic chemical vapor deposition (MOCVD) technique to provide high quality films on large-area substrates for fundamental studies and device applications. MOCVD is currently the dominant technique in the deposition of large-area device quality III-V and II-VI compounds.[13] Despite its promise, MOCVD has not been utilized so far in the deposition of the high T_c superconducting films, except in a preliminary attempt.[14]

Here we report our recent studies on high-temperature superconducting films deposited by MOCVD. Our results show that after post-annealing, highly oriented single phase superconducting $YBa_2Cu_3O_{7-x}$ films can be obtained reproducibly with a transition onset temperature at 93 K and a zero resistance temperature at 84 K on yttria-stabilized zirconia (YSZ) (100) substrates. Although they still show a single phase $YBa_2Cu_3O_{7-x}$ structure under similar processing conditions, films deposited on sapphire ($1\bar{1}02$) usually have a very broad superconducting transition with zero resistance at much lower temperature (10–40 K).

Metal β-diketonates such as $Y(C_{11}H_{19}O_2)_3$, $Ba(C_{11}H_{19}O_2)_2$, and $Cu(C_{11}H_{19}O_2)_2$ were used as the metalorganic precursors. Individual precursor sources were wrapped with heating tapes and maintained at 160, 300, and 170 °C for the Y, Ba, and Cu compounds, respectively. The main gas manifold was heated to 300 °C to eliminate the condensation of the reactants upstream. Argon was used as the carrier gas at flow rates of 250 sccm for Y, 1950 sccm for Ba, and 320 sccm for Cu. By carefully controlling the flow rates and heating temperatures, the precursors were evaporated and carried by argon gas to the reactor after premixing with oxygen gas which was at a flow rate of 1950 sccm. A warm wall vertical reactor made of stainless steel was used with a resistive heating stage for the deposition. The temperature of the susceptor was set at 650 °C and the reactor pressure was kept at about 50 Torr during the deposition. The partial pressures for the Y, Ba, and Cu precursors were estimated to be 3, 11, and 10 Torr, respectively. After one hour of deposition at a rate of 10 μm/h, the films were cooled to room temperature under oxygen flow. The as-deposited films were black and had high resistivity. The optimum post-annealing conditions under oxygen flow were 950 °C for 30 min for the films deposited on YSZ, and 895 °C for 15 min for the films deposited on sapphire. After the high-temperature anneals the samples were cooled slowly (about 4 °C/min) to ambient temperature.

The structure of the films was analyzed by using x-ray diffraction and the surface morphology was examined by scanning electron microscopy (SEM). The composition of the films was checked by using the energy dispersive spectroscopy (EDS) technique. The films on YSZ after post-annealing had the composition of 1:2:3 phase to within 1% as compared to a bulk standard sample. For x-ray diffraction, a digitized horizontal diffractometer from Siemens with a Ni-filtered Cu $K\alpha$ radiation was used. Four-terminal low-frequency ac resistivity measurements were made with indium pressure contacts.

Figures 1(a) and 1(b) show surface and cross-section SEM micrographs, respectively, of an as-deposited film on YSZ substrate. As can be seen, the surface is fairly rough and the film consists of an aggregation of micron-size particles. The film seems to be highly porous, possibly due to homogeneous nucleation in the gas phase. Figures 2(a) and 2(b) show surface and cross-section SEM micrographs, respectively, of the same film after post-annealing at 950 °C for 30

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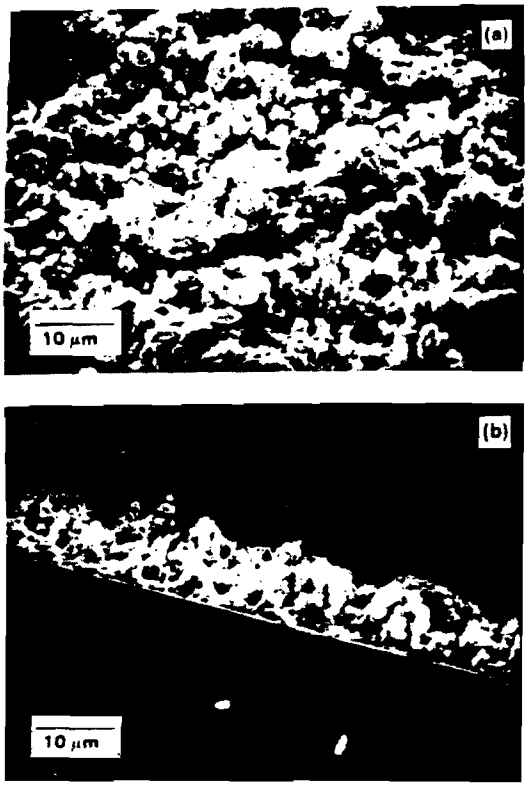

FIG. 1. SEM micrographs of (a) the surface and (b) the cross section for an as-deposited film on YSZ.

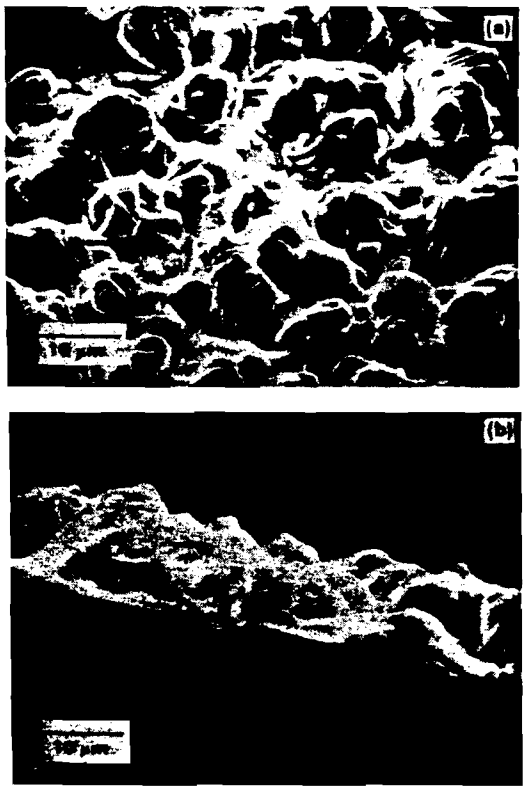

FIG. 2. SEM micrographs of (a) the surface and (b) the cross section for the film on YSZ after post-annealing at 950 °C for 30 min.

min. The post-annealing greatly improves the surface morphology and eliminates the porosity, providing a dense film. No cracking or peeling was observed in the films examined with thicknesses as high as 10 μm. Similar results were obtained for the films deposited on sapphire substrates.

The x-ray diffraction pattern of an as-deposited film on YSZ is shown in Fig. 3(a). This pattern shows that the as-deposited film is a mixture of yttrium oxide, copper oxide, and barium carbonate. Electron microprobe analysis provides evidence that the mixture is homogeneous at submicron level. Similar results were obtained for the films deposited on sapphire. In Fig. 3(b), the diffraction pattern shows that, after post-annealing, the film on YSZ has a single phase orthorhombic $YBa_2Cu_3O_{7-x}$ structure. This conclusion is drawn by comparing the thin-film pattern in Fig. 3(b) to the pattern in Fig. 3(c) obtained from a powdered bulk superconducting $YBa_2Cu_3O_{7-x}$ sample. The pattern for the film shows that all the (00l) lines have very pronounced intensity, indicating a highly textured structure with the c-axis oriented perpendicular to the substrate surface. It is remarkable that films with thicknesses as large as 10 μm can be grown almost completely textured. Highly textured films are important because of the large critical currents they can carry.[3,11] In Fig. 3(b), there are two extra peaks, which cannot be associated with the $YBa_2Cu_3O_{7-x}$ structure. The peak at 35° comes from the YSZ substrate. The peak at 43° can be attributed to $BaZrO_3$ compound forming at the interface due to the reaction between the film and the substrate.[15]

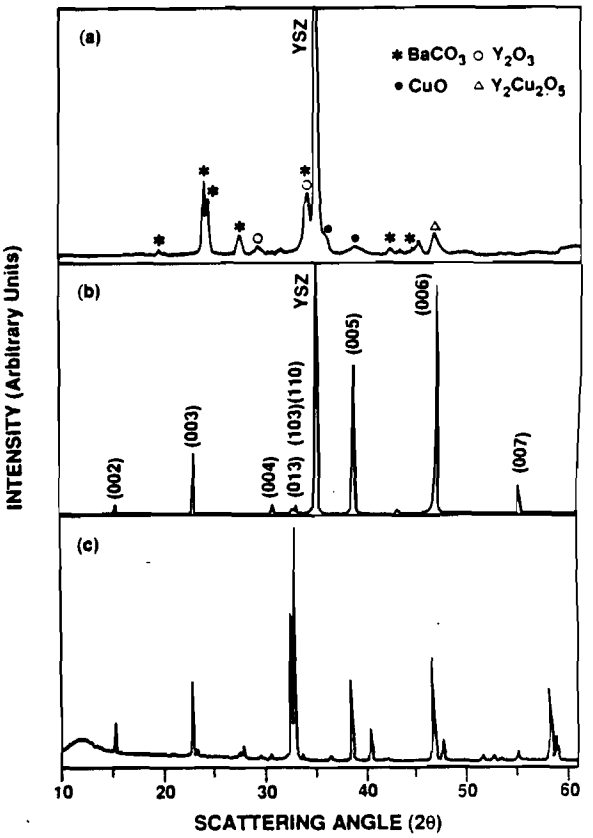

FIG. 3. X-ray diffraction patterns for the samples (a) as-deposited on YSZ, (b) post-annealed at 950 °C for 30 min, and (c) the powdered bulk $YBa_2Cu_3O_{7-x}$ superconductor.

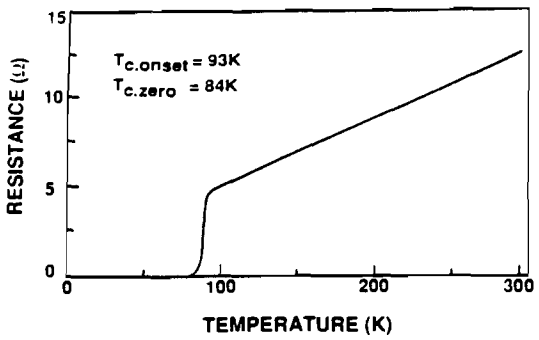

FIG. 4. Resistance as a function of temperature for a post-annealed $YBa_2Cu_3O_{7-x}$ film deposited on YSZ.

Figure 4 shows the result of the resistivity measurements as a function of temperature for a film deposited on YSZ. The contact resistances were 20 Ω and 200 Ω for films on YSZ and sapphire, respectively. The film on YSZ in Fig. 4 shows a sharp transition with an onset of 93 K, zero resistance at 84 K, and a width (10–90%) of 4 K. The resistivities of the films on YSZ substrates are about $4.5\times10^{4}\,\mu\Omega$ cm at room temperature. The resistivity of the film on YSZ decreases linearly from room temperature to the transition onset with $\rho_{300\,K}/\rho_{95\,K}$ value to be 2.6 indicating good metallic behavior in the normal state. The resistivity of the films deposited on sapphire exhibits semiconducting behavior in the normal state. This film has a resistance peak value just above the superconducting transition. The zero resistance temperature is as low as 10 K indicating a strong interaction between the sapphire substrate and the film.

In summary, a highly textured single phase $YBa_2Cu_3O_{7-x}$ thin film has been obtained by the MOCVD technique on YSZ (100) substrates with a sample thickness as large as 10 μm. SEM shows a dense recrystallized homogeneous $YBa_2Cu_3O_{7-x}$ film after post-annealing at 950 °C for 30 min. X-ray diffraction indicates a mixture of metal oxides and carbonates for the as-deposited films and a c-axis highly oriented single phase $YBa_2Cu_3O_{7-x}$ with orthorhombic structure for the post-annealed ones. Resistivity measurements show good metallic behavior in the normal state for the film deposited on YSZ with a superconducting onset temperature of 93 K and a zero resistance temperature of 84 K.

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Metalorganic chemical vapor deposition of [100] textured MgO thin films

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We report on the results of a recent study on the deposition of [100] textured MgO films on fused quartz substrates by using the metalorganic chemical vapor deposition technique. Magnesium β-diketonate was used as the metal source and the growth rate of the film was about 0.4 μm/h at 740 °C in a horizontal warm wall reactor. X-ray diffraction experiments provided evidence that the MgO films on fused quartz were fully textured with [100] orientation perpendicular to the substrate surface. The films had a very smooth surface morphology and optical transparency with an index of refraction of 1.71.

The growth of highly textured polycrystalline thin films on amorphous substrates is of great scientific interest in addition to obvious practical applications. The mechanism for the selection of orientations and the growth forms are not well understood even though various models have been proposed.[1] For practical purposes, these textured films can be used as buffer layers to deposit other oriented films on top. In this letter, we report, for the first time, the growth of [100] oriented MgO films on fused quartz substrates by using the metalorganic chemical vapor deposition (MOCVD) technique. These films will be used as large-area substrates for depositing oriented high T_c superconducting thin films.[2-4]

Attempts to deposit superconducting thin films directly on Si and amorphous SiO_2 have been unsuccessfully because of severe interdiffusion and rearrangement of the constituents.[5,6] However, c-axis oriented $YBa_2Cu_3O_x$ films have been successfully deposited on Si(100) with buffer layers of (111) textured MgO and (100) textured ZrO_2.[7] In these studies, both the superconducting thin films and the buffer layers were grown by the rf magnetron sputtering technique. We have focused our research efforts on the development of MOCVD technique to provide high quality films on large-area substrates for fundamental studies and devices applications. MOCVD is currently the dominant technique in the deposition of large-area device quality III-V and II-VI compounds.[8]

The schematic diagram of the MOCVD apparatus used has already been reported elsewhere.[9] It consists of a stainless-steel source chamber which contained the metalorganic precursor, a mixing chamber with an auxiliary outlet, and a horizontal warm quartz reaction chamber with stainless-steel susceptor. The reaction chamber had an inner diameter of 50 mm. The susceptor was heated using a shell-shaped resistive heating element, and the temperatures of the source chamber and the lines were controlled by heating tapes.

We have chosen magnesium β-diketonate, $Mg(thd)_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedione), as the metalorganic precursor and argon as the carrier gas. Additional oxygen was necessary to eliminate carbon incorporation in the film. 25 mm × 25 mm fused quartz plates and Si(100) wafers were used as the substrates.

Growth parameters greatly affected the degree of texturing of the MgO thin films. Therefore, we have kept the flow rates of the carrier gases and the reactor total pressure constant to study the effects of the source temperature (T_{so}), the substrate temperatures (T_{su}), and the growth time. The flow rates of argon and oxygen were 1000 and 500 sccm, respectively. The reactor total pressure was one atmosphere. For the growth of 100% [100] textured MgO thin films on fused quartz, the following parameters were used: $T_{su} = 740$ °C, $T_{so} = 195$ °C, and the growth time of 1 h. The gas manifolds and the reactor walls were heated to 20°–30° higher than the source temperature to eliminate the condensation of the reactants upstream. Under the conditions above, the $Mg(thd)_2$ partial pressure in the reactor was 0.23 Torr.

The structure of the as-grown MgO thin films was analyzed by using x-ray diffraction, both scanning and transmission electron microscopies, ion channeling and Rutherford backscattering (RBS) technique. For x-ray diffraction, a digitized horizontal diffractometer from Siemens with a Ni-filtered Cu $K\alpha$ radiation was used. By using ellipsometry, the index of refraction of the MgO thin film grown on Si(100) was determined to be 1.71 as compared to bulk value of 1.736.

Figure 1 shows the mass transport and the growth rates

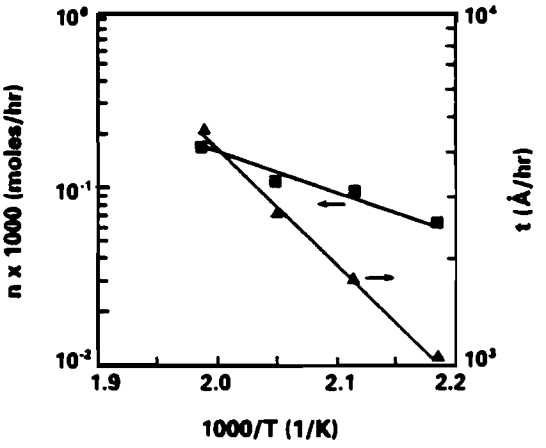

FIG. 1. Mass transport (squares) and growth rates (triangles) in the log scale as a function of the inverse source temperature.

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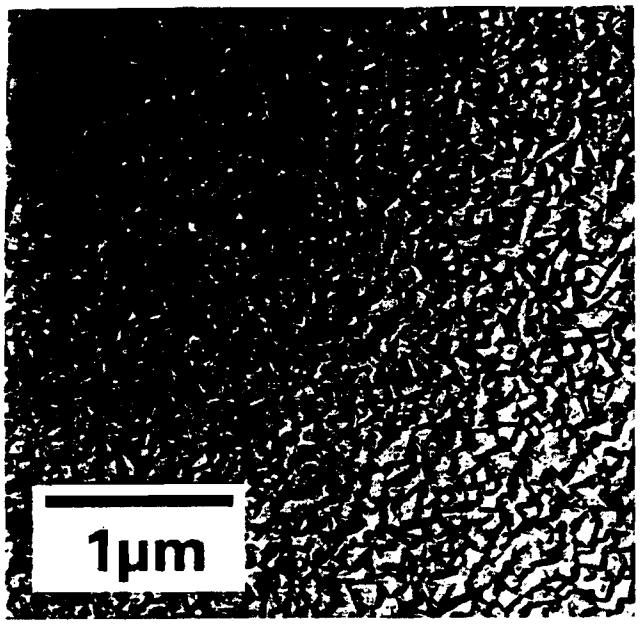

FIG. 2. Transmission electron micrograph of a replica of the surface of MgO thin film on quartz: T_{su} = 740 °C and T_{ox} = 195 °C.

in the log scale as a function of the inverse source temperature of the $Mg(thd)_2$ with the T_{su} at 740 °C. The figure suggests that we are operating in the surface kinetic limited regime because the mass transport rate and the growth rate have different activation energies.[10]

The MgO thin films produced were transparent and showed no apparent peeling. Transmission electron micrograph of the replica of the surface is shown in Fig. 2, with a magnification of 45 000. There exist some faceted hillocks and pits in this length scales, but it does not exhibit any features which can be attributed clearly to cracks or pinholes.

Figure 3 shows the RBS spectrum for a MgO film on fused quartz. The solid line is a simulation of MgO/SiO_2 using the RUMP program.[11] The composition of the film is that of MgO within the error (5%). The thickness of the film was determined to be 4500 Å corresponding to a growth rate of 0.45 μm/h. In Fig. 3, the foot in the spectrum above the Mg position is due to the isotropic effect and is well

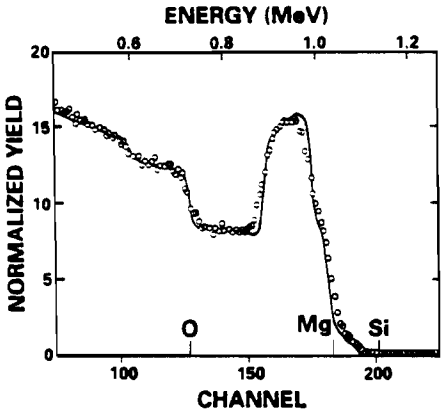

FIG. 3. RBS spectrum (circle) for a MgO film on fused quartz. The solid line is a simulation of 4500-Å-thick MgO/SiO_2.

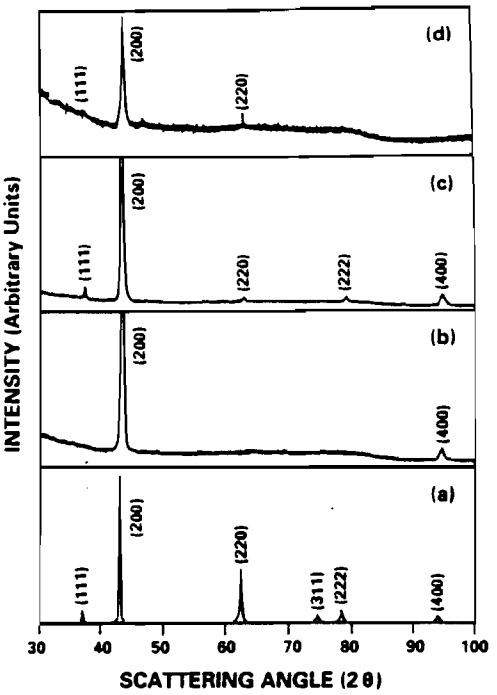

FIG. 4. X-ray diffraction patterns of (a) powdered single-crystal MgO, (b) MgO/quartz with T_{su} = 740 °C, T_{ox} = 195 °C, and 1 h growth, (c) MgO/quartz; same as in (b) except for 2 h growth, and (d) same as in (b) except for T_{su} = 650 °C. Note that the vertical axes of (b) and (c) have been expanded by factor of 5 to accentuate the intensity ratios.

described by the simulation. In the ion channeling mode, there was no detectable channeling. This suggests that the mosaic spread in the film in the [100] orientation is larger than the channeling angular width (about 1°).

Figures 4(a) and 4(b) respectively show the diffraction patterns of a powdered single-crystal MgO (average particle size was about 40 μm) and a MOCVD-grown MgO thin film on fused quartz plate. By comparing Figs. 4(a) and 4(b), we conclude that the MgO thin film is 100% [100] textured. Figure 4(c) shows the diffraction pattern of MgO on quartz grown at the same conditions as above except for the growth time of 2 h. One can clearly see the loss of perfect texturing as the deposition time is increased. Figure 4(d) shows the diffraction pattern of the MgO on quartz grown under the same conditions as in Fig. 4(b) except T_{su} was at 650 °C. Once

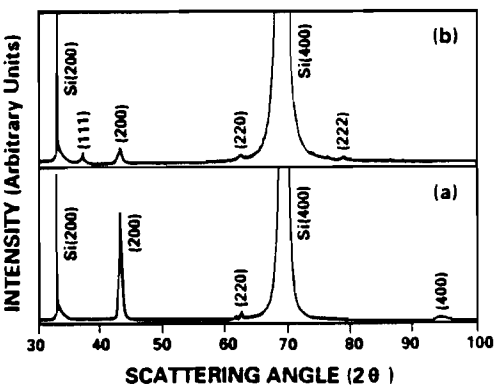

FIG. 5. X-ray patterns of MgO/Si(100) with T_{ox} = 195 °C. (a) T_{su} = 650 °C and (b) T_{su} = 740 °C.

again, one can see the loss of perfect texturing. These results suggest that the texturing is caused by the preference for a certain set of crystal plane to nucleate parallel to the amorphous smooth substrate within a certain substrate temperature range, as discussed by van der Drift.[1]

Figures 5(a) and 5(b) show the diffraction patterns of the MgO thin film on Si(100) with T_{su} at 650 and 740 °C, respectively. Unlike the deposition on fused quartz, there exists a greater degree of [100] texturing in the film grown at lower substrate temperature on Si(100). In fact, the film grown at $T_{su} = 740$ °C has [111] preferred orientation as evidenced by the increase in the intensity ratio of (111)/(200) as compared to the powder. This is similar to the results obtained for MgO films deposited on Si(100) by rf magnetron sputtering at 700 °C.[7]

In summary, high quality [100] textured MgO thin films on fused quartz plates and Si(100) have been grown successfully by using MOCVD. The films obtained were densely packed and had good surface morphology. Rutherford backscattering showed that the film is stoichiometric MgO. Index of refraction of the MgO films on Si(100) is 1.71. It appears, for the fused quartz plate, that the texturing is caused at the initial nucleation stage where (100) planes form parallel to the smooth amorphous substrate, which loses the orientation sharpness during the vertical growth stage. Next, we intend to deposit superconducting thin films on these textured MgO buffer layers using both MOCVD and laser ablation techniques.

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Metalorganic chemical vapor deposition of $PbTiO_3$ thin films

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$PbTiO_3$ thin films have been grown successfully for the first time by using purely metalorganic precursors, namely, titanium isopropoxide and tetraethyllead. A scanning electron micrograph showed dense and noncolumnar growth with good surface morphology. Temperature-dependent x-ray diffraction studies provide evidences for a reversible tetragonal to cubic phase transition around 540 °C. At room temperature, the dielectric constant is about 180.

Lead titanate is a well known perovskite type ferroelectric material with a large spontaneous polarization, and a small dielectric constant.[1] Possible applications to electronic and optical devices have brought much attention to the method of preparation of pure $PbTiO_3$ thin films. Most of the ferroelectric thin films grown to date have been fabricated by either rf sputtering or chemical vapor deposition (CVD).[2–4] However, as pointed out by Nakagawa *et al.*,[3] the rf sputtering method has obvious disadvantages, such as low deposition rate, generation of surface defects, surface roughness, and stoichiometric changes in film from source materials. The conventional CVD method, although it eliminates the disadvantages of rf sputtering, has its own disadvantages compared to the metalorganic chemical vapor deposition (MOCVD) method. The MOCVD method generally provides: (1) flexible control of deposition by simple control of the flow rates, (2) generally higher vapor pressure of metalorganics compared to metal halides, (3) deposition at lower temperatures, (4) ideal adaptability for multiple component and layer deposition, and (5) straightforward scaling up to commercial production volumes.[5] Moreover, unlike the CVD apparatus of Nakagawa *et al.*,[3] all experimental parameters can be independently controlled; in particular, the reactor temperature and the vapor pressure of the precursors are independent. We therefore have performed a series of experiments to explore the possibility of using MOCVD in the fabrication of ferroelectric thin films.

In this letter, we report the results of the first MOCVD-grown $PbTiO_3$ thin films from purely metalorganic precursors. The schematic diagram of the MOCVD apparatus used is shown in Fig. 1. It consists of bubblers which contain metalorganic precursors, a mixing chamber with an auxiliary outlet, and a horizontal warm wall quartz reaction chamber with a graphite susceptor. The reaction chamber had an inner diameter of 50 mm. The susceptor was heated using a shell-shaped resistive heating element, and the temperatures of the bubblers and lines were controlled by heating tapes. Pressure is controlled by metering valves and monitored by differential pressure gauges.

We have chosen tetraethyllead (TEPB) and titanium isopropoxide (TIP) as the metalorganic precursors and argon as the carrier gas. No additional oxygen in the carrier gas was necessary to grown $PbTiO_3$ and all the oxygen was derived from TIP. 25×25 mm fused quartz plates were used as the substrates. The substrate temperature was kept at 500 °C. The gas manifolds and the reactor walls were heated to 100 °C to eliminate the condensation of the reactants upstream. No deposition was observed on the walls due to warmup. The flow rates of the carrier gas were 2000 sccm for TIP and 700 sccm for TEPB with reactor total pressure at 100 Torr. The bubbler temperatures were set at 45 and 25 °C for TIP and TEPB, respectively. Under the conditions above, the TIP partial pressure was 0.37 Torr and the TEPB partial pressure was 0.093 Torr.

The structure of the as-grown $PbTiO_3$ thin films was analyzed using x-ray diffraction and scanning electron microscopy (SEM). For x-ray diffraction, a digitized horizontal diffractometer from Siemens with a Ni-filtered Cu K_α radiation was used. A high-temperature stage with Ni-chrome heating was utilized at elevated temperatures. A chromel-alumel thermocouple was placed right under the center of the sample for temperature measurement. The dielectric constant was measured by using interdigital electrodes and an impedence bridge. The dielectric constant was calculated from measured capacitance of the interdigital electrodes.[6,7]

The lead titanate thin films produced were conducting, grayish in color, and showed no apparent peeling which indicated that there was an insignificant amount of internal stress. Figure 2 shows a scanning electron micrograph of the film in cross section. As can be seen, it is densely packed, has no apparent columnar growth, and has reasonably good surface morphology. The growth rate was 6.4 μm/h under the conditions specified above.

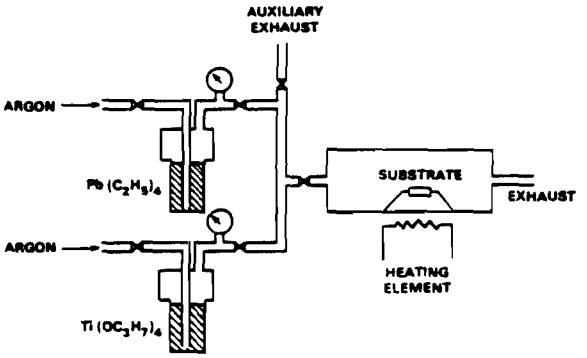

FIG. 1. Schematic diagram of the MOCVD apparatus used for $PbTiO_3$ growth.

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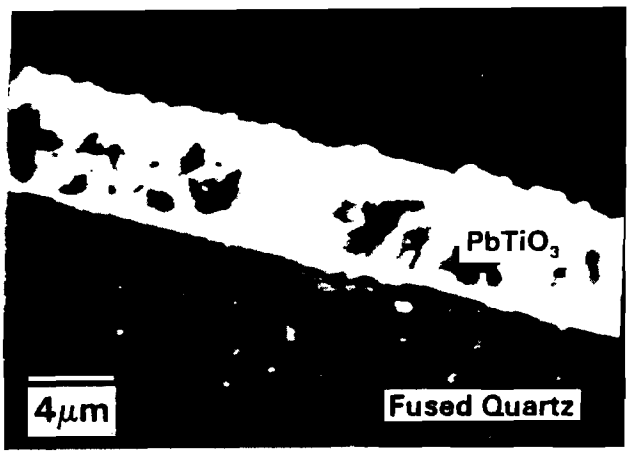

FIG. 2. Cross-sectional scanning electron micrograph of $PbTiO_3$ on fused quartz plate.

Figure 3 shows the diffraction pattern of a powdered bulk $PbTiO_3$ and of a MOCVD-grown $PbTiO_3$ thin film on fused quartz plate. All peaks that are present in the thin film are also present in the powder, indicating the presence of a pure phase $PbTiO_3$ thin film. However, there exists strong texturing in the [100] direction. This is evident from the intensity ratio of (100) to (001) peaks. A [100] texture direction indicates that the *c* axis, and therefore the spontaneous polarization vector, is parallel to the plane of the substrate. By contrast, sputter-deposited $PbTiO_3$ thin films on Pt exhibit a spontaneous polarization vector perpendicular to the plane of the substrate.[2]

The results of x-ray diffraction experiments as a function of temperature are shown in Fig. 4. In the heating cycle, one can see clearly that the separation between (001) and (100) peaks decreases as the temperature increases. The transition is complete at 545 °C and is reversible as evidenced by the cooling cycle. However, there is about 10 °C hysteresis between the cycles.

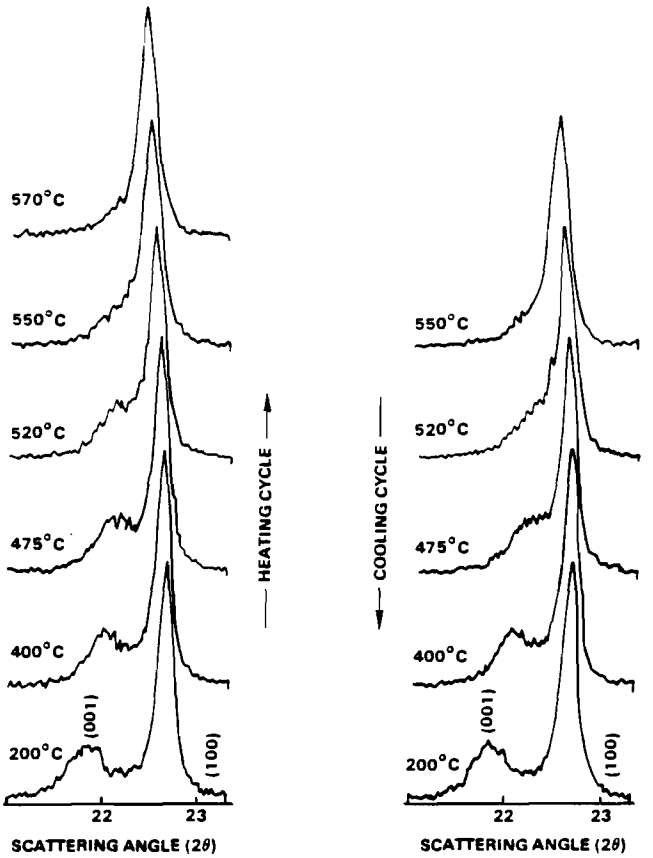

FIG. 4. High-temperature x-ray diffraction patterns of the $PbTiO_3$ film, grown at 500 °C substrate temperature.

The results of these high-temperature x-ray diffraction experiments were used to obtain the temperature dependence of the lattice parameters *a* and *c*, which are plotted in Fig. 5. We thus observe a phase transition from a tetragonal

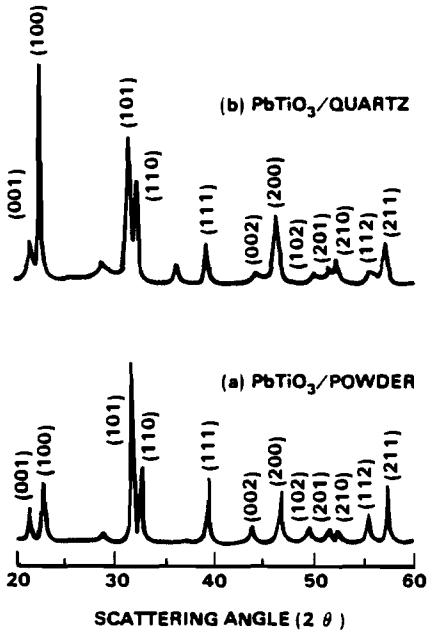

FIG. 3. X-ray diffraction pattern of (a) powdered bulk $PbTiO_3$ (b) $PbTiO_3$ film grown by MOCVD at substrate temperature of 500 °C. Note the [100] texture direction in the $PbTiO_3$ thin film.

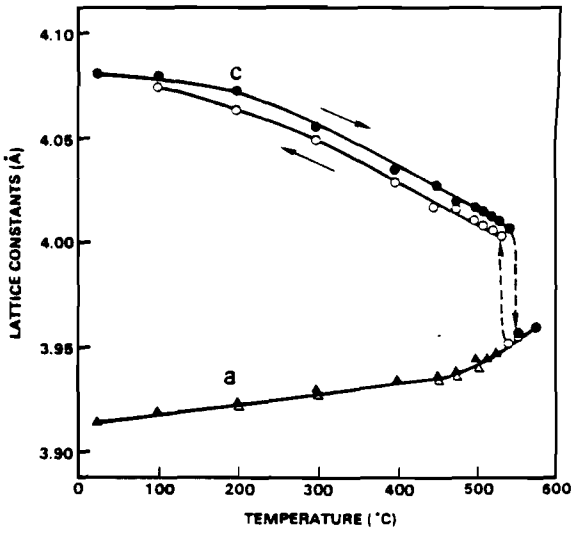

FIG. 5. Temperature dependence of the lattice constants *a* and *c*. The light and dark points show the data points during the cooling and heating cycles, respectively.

to a cubic phase upon heating at 545 °C and the reverse transition at 535 °C upon cooling, indicating substantial hysteresis. The corresponding phase transition from the tetragonal to the cubic phase in the bulk $PbTiO_3$ takes place at 499 °C. The shift of the Curie temperatures to higher values in the thin films has been also observed in various other ferroelectric compounds.[2,8,9] It may be attributed to the stabilization of the ferroelectric phases by the substrates. The change in the *a*-axis parameter with temperature is almost the same in both heating and cooling whereas the *c* axis exhibits hysteresis. Similar broadening and hysteresis were reported in sputter-deposited $PbTiO_3$ thin films in the first temperature cycling.[2] However, the hysteresis in our films was not affected by subsequent heatings.

At room temperature the dielectric constant of the MOCVD-grown $PbTiO_3$ film was about 180 as compared to the bulk value of 210.

In summary, high quality $PbTiO_3$ thin films on fused quartz plate have been grown successfully using MOCVD. Thus the MOCVD technique is a viable alternative in growing $PbTiO_3$ and presumably other multiple component oxide thin films. The films obtained were conducting, densely packed, without columnar growth, and showed strong [100] texture direction. The dielectric constant at 25 °C is 180. The tetragonal to cubic phase transition observed in the MOCVD-grown thin films exhibited hysteresis and considerable displacement of the Curie temperature relative to its bulk value. Next, we plan to grow the films epitaxially on single-crystal substrates.

The authors would like to acknowledge helpful discussions with A. Zangwill and R. A. Young, and assistance from J. Cagle for the x-ray experiments. This work was sponsored by the U.S. Army and the Alfred P. Sloan Foundation.

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Metalorganic Chemical Vapor Deposition of $Tl_2CaBa_2Cu_2O_y$ Superconducting Thin films on Sapphire

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Abstract

Superconducting $Tl_2CaBa_2Cu_2O_y$ thin films have been successfully grown on the single crystal sapphire $(1\bar{1}02)$ substrate by using the Metalorganic Chemical Vapor Deposition technique. The growth rate of the films was about 5 μm/hr. The as-deposited film was post-annealed in a partially sealed ceramic crucible in the presence of a $Tl_2Ca_2Ba_2Cu_3O_y$ pellet to achieve the superconducting phase. The x-ray data show strong diffractions from the $Tl_2CaBa_2Cu_2O_y$ superconducting phase in addition to the trace amounts of Ca_2CuO_3 and $BaCO_3$. Superconducting transition temperatures with onset above 100 K and zero resistance at 94 K can be obtained by further heat treatment at 500°C in oxygen.

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The Tl-Ca-Ba-Cu-O system represents a class of superconducting materials with transition temperatures as high as 125 K.[1-3] The high transition temperatures coupled with the high critical current densities observed in this system make these materials better suited to practical device applications. However, the preparation of Tl-based superconducting materials presents a challenge because of the toxicity and volatility of thallium. Superconducting thin films of these materials have been obtained by several deposition techniques, including magnetron sputtering,[4-7] RF diode sputtering,[8,9] electron beam evaporation,[10] spin coating,[11] sequential thermal evaporation,[12] and pulsed laser evaporation.[13] Our research effort focuses on the development of the metalorganic chemical vapor deposition (MOCVD) technique to provide high quality films on large-area substrates for fundamental studies and device applications. Since the MOCVD technique does not require a high vacuum, the volatility of thallium oxide may be used as an advantage for the in-situ preparation of the Tl-based superconducting thin films. We have used sapphire as the substrate because of its low dielectric constant and dielectric loss, which are important properties for high-frequency application. In addition, sapphire is cheap and available with large areas.

In this letter, we report the deposition of high temperature superconducting films of Tl-Ca-Ba-Cu-O system by the MOCVD technique. Our results show that after post-annealing of the as-deposited film in the presence of a 2223 pellet, the $Tl_2CaBa_2Cu_2O_y$ superconducting phase can be reproducibly obtained with a zero-resistance temperature at 94 K on sapphire $(1\bar{1}02)$ substrates.

2,2,6,6 -tetramethyl - 3, 5 -heptanedione (thd) metal β -diketonates, such as, Tl(thd), $Ca(thd)_2$, $Ba(thd)_2$ and $Cu(thd)_2$ were used as the metalorganic precursors. The apparatus utilized for the deposition is the same as the one used for $YBa_2Cu_3O_{7-x}$ film deposition[14] except an additional line for the Tl precursor. The individual metalorganic precursors held in quartz crucibles were wrapped with heating tapes and kept at 165, 255, 285 and 160°C, respectively, for the Tl, Ca, Ba, and Cu precursors. The main gas manifold was kept at about 300°C in order to avoid any condensation of the gaseous reactants. Argon was used as the carrier gas with flow rates of 500 sccm for Tl and Ba, 85 sccm for Cu and Ca. The gas carrying the precursors was

premixed with oxygen, which had a flow rate of 100 sccm, before entering into the reactor. An auxiliary outlet was used to avoid the deposition during the initial surge and unsteady gas flow. A warm wall vertical reactor made of stainless steel was used with a resistive heating stage for the deposition. A pressure gauge was directly attached to the reactor chamber for the measurement of the reactor pressure. The susceptor temperature was controlled at 600°C and the reactor pressure was kept at about 50 torr during the deposition. Under the conditions mentioned above, a film deposition rate of 5 μm/hr was obtained. After the deposition step the source lines were closed and the film was cooled to room temperature under oxygen flow. Polished sapphire wafers with the $(1\bar{1}02)$ orientation were used as substrates.

Some basic studies on the MOCVD deposition process have already been reported for the $YBa_2Cu_3O_{7-x}$ system[14]. Here, in order to understand the deposition process further, we have carried out a systematic study of the mass transport rates for the precursors as a function of the deposition time. The results are shown in Figure 1(a) and (b). These experiments were performed with fixed condition as follows, the reactor temperature at 600°C, pressure at 50 torr, gas flow rates at 500 sccm for Tl, Ba and at 85 sccm for Cu, Ca precursors. The metalorganic source temperatures were at 165, 160, 255 and 285°C for Tl, Cu, Ca and Ba precursors, respectively. The starting chemical weights were at 0.5 grams for Cu and Ba, 0.6 grams for Tl and 0.4 grams for Ca, respectively. The transport time was started after the stabilization of the initial surge and unsteady gas flow. This should explain the zero offset in the figures. As can be seen, under deposition condition specified, the Cu and Ca precursors exhibit a linear behavior throughout the one-hour deposition time, while the data for Tl and Ba show a saturation after about 30 minutes. This could be explained in two possible ways. First explanation might be that at the source temperatures used, the metal precursors start to decompose and loose volatility after about 30 minutes. Second possibility is that most of the usable precursors were consumed within the first 30 minutes and remaining is just some residue compound. This study is still being continued for various deposition parameters to establish the optimum deposition conditions for high quality films.

The as-deposited films were dark-brown and had very high contact resistance. These films

were not as porous as the one observed in the $YBa_2Cu_3O_{7-x}$ system.[15] The post-annealing process was studied as a function of temperature, oxygen partial pressure and Tl-vapor environment. The results show that the superconductivity of the films is extremely sensitive to the different annealing conditions. The best results were obtained for the films annealed at 850°C in air for 40 minutes in the presence of a pressed 2223 pellet in a partially sealed crucible and then quenched to room temperature. The zero-resistance transition temperature can be improved by further annealing the sample at 500°C in oxygen for several hours followed by furnace cooling.

The microstructure and the surface morphology of the films were examined by scanning electron microscopy (SEM). The structure of both as-deposited and post-annealed films were examined by using a digitized horizontal x-ray diffractometer from Siemens with a Ni-filtered Cu K_α radiation. Resistivity as a function of temperature was measured in a close-cycle refrigerator by using the standard four-point low frequency AC measurements. A Si-diode thermometry traceable to the NBS standards with one Kelvin accuracy was used over the temperature range measured. Electron microprobe analysis indicates that, generally, the as-deposited films are Tl deficient as compared to the 2122 composition. Therefore, post-annealing under a Tl-rich environment is necessary to achieve the superconducting phase.

Figures 2(a) and (b) show the surface and cross-section SEM micrographs of a film after post-annealing. It can be seen that the surface morphology is somewhat better than that of the $YBa_2Cu_3O_{7-x}$ case reported earlier.[15] No cracking or peeling was observed in the films with thicknesses as high as 5μm.

In the as-deposited films, when Ba/Ca ratio is high, the x-ray diffraction always shows the presence of $BaCO_3$ along with CuO, $BaCuO_2$ and Ca_2CuO_3. As the Ba/Ca ratio is decreased, the $BaCO_3$ phase is reduced. Within a certain range of the Ba/Ca ratio near 2122 composition, the $BaCO_3$ phase can be totally eliminated even at reactor temperatures as low as 600°C. Figure 3 shows the x-ray diffraction pattern for the same post-annealed sample analyzed with SEM. In Fig. 3, it can be seen that the diffraction peaks are sharp, indicating a well crystallized structure, and the dominant phase is the $Tl_2CaBa_2Cu_2O_y$ superconducting phase. In addition to the major

2122 phase, trace amounts of $BaCO_3$ and Ca_2CuO_3 can also be observed.

Figure 4 shows the result of resistivity measurements as a function of temperature. The curve (b) is for a sample post-annealed in air at 850°C for 40 minutes. The curve (a) is for the same sample after annealing it further at 500°C for 6 hours under oxygen flow followed by furnace cooling. It is clear that low temperature annealing under oxygen does help to raise $T_{c(R=0)}$ several degrees higher, indicating that oxygen vacancies and orderings in this system is important to superconductivity. In normal state, both measurements show similar metallic behavior as a function of temperature. However, the normal state resistance is higher for the sample annealed second time at low temperature under oxygen flow. This implies some loss of thallium in this sample. The loss of thallium may be avoided by introducing thallium vapor into the flow during the second annealing process.

In summary, the superconducting $Tl_2CaBa_2Cu_2O_y$ thin films by MOCVD technique have been obtained on sapphire $(1\bar{1}02)$ substrates with a thickness of about 5 μm. SEM study shows a dense film without cracking or peeling. X-ray diffraction shows that within a certain range of the Ba/Ca ratio near the 2122 composition by careful control of the deposition parameters, $BaCO_3$ phase could be eliminated from the as-deposited film. After a post-annealing at high temperatures under Tl vapor, a well-crystallized $Tl_2CaBa_2Cu_2O_y$ phase can be formed. The R-T measurements show that a zero resistance temperature at 94 K can be achieved after a second post-annealing in oxygen at 500°C and furnace cooling.

The authors would like to acknowledge helpful discussion with R.A.Young, and assistance from J. Cagle and G. Freeman for the x-ray experiments and electron microscopy, respectively. This work was sponsored by the Department of Energy. A. Erbil acknowledges an Alfred P.Sloan Research Fellowship.

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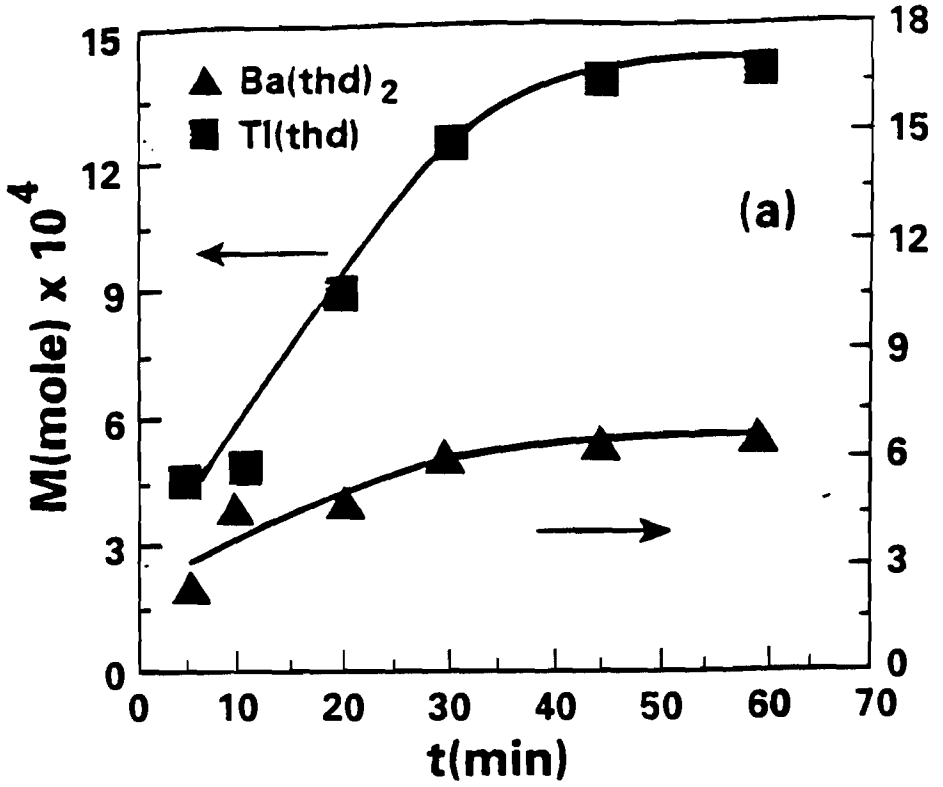
Figures Caption

Figure 1. Mass transport rates as a function of deposition time for the metal precursors of (a) Ba, Tl , and (b) Cu, Ca.

Figure 2. SEM micrographs of (a) the surface and (b) the cross section for a film on sapphire post-annealed at 850°C for 40 minutes in air followed with further treatment at 500°C for 6 hours in O_2.

Figure 3. X-ray diffraction pattern for the same sample analyzed by SEM in Figure 2. "S" sign in the figure refers to the diffraction peaks from the sapphire substrate

Figure 4. Resistance as a function of temperature for a $Tl_2CaBa_2Cu_2O_y$ thin film on sapphire post-annealed at 850°C in air for 40 minutes (b), and followed by further treatment at 500°C for 6 hours in O_2 (a).


Ba(thd)2
Tl(thd)
(a)
M(mole) x 10^4
t(min)
0
3
6
9
12
15
18
0
10
20
30
40
50
60
70

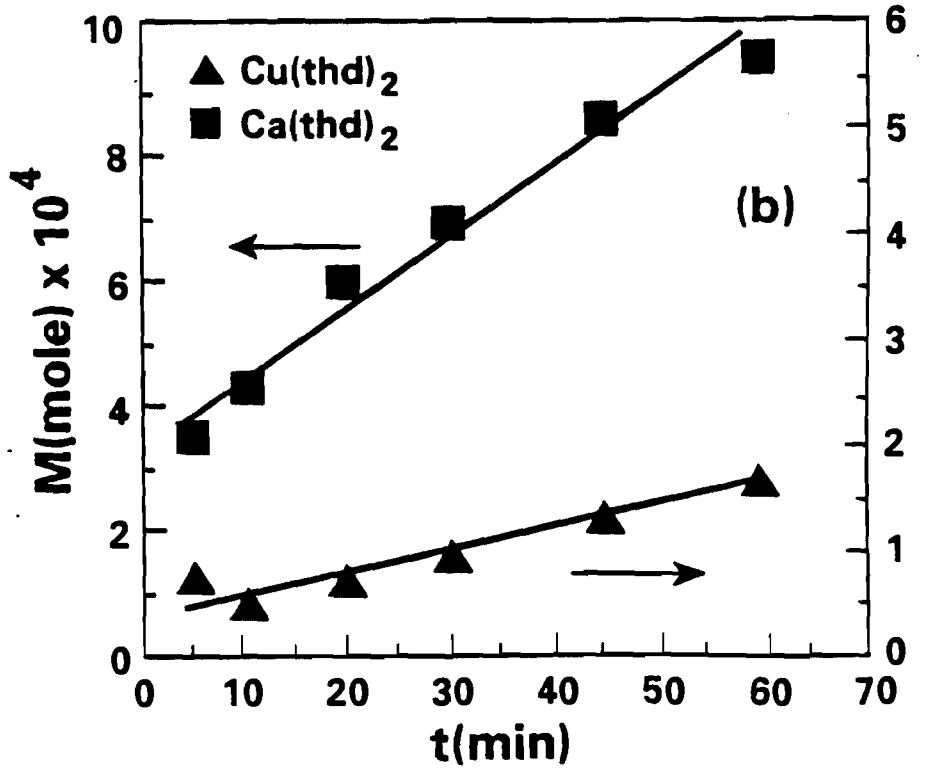
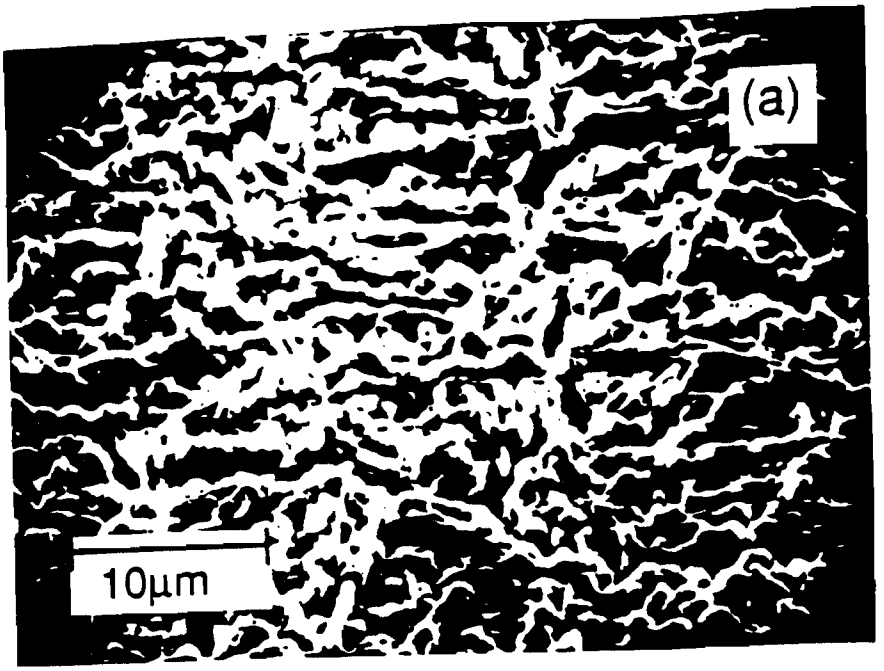

Cu(thd)2
Ca(thd)2
(b)
M(mole) x 10^4
t(min)
0
2
4
6
8
10
0
1
2
3
4
5
6
0
10
20
30
40
50
60
70

Fig. 1



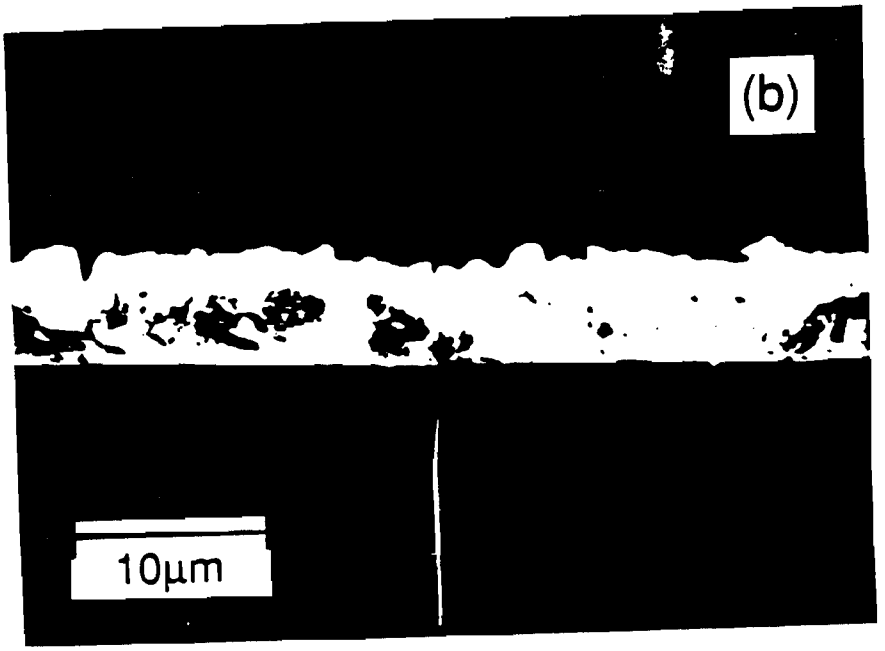


Fig. 2

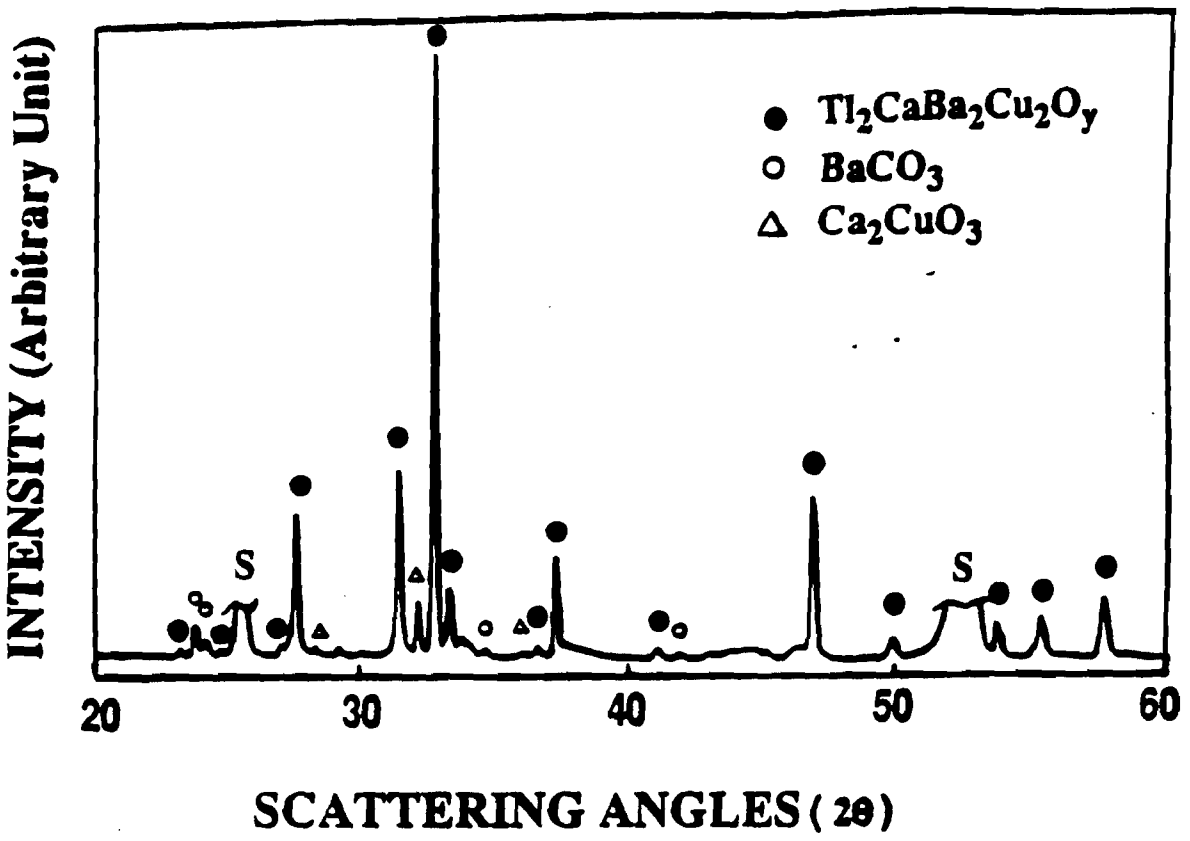

INTENSITY (Arbitrary Unit)
● $Tl_2CaBa_2Cu_2O_y$
○ $BaCO_3$
△ Ca_2CuO_3
S
S
20
30
40
50
60
SCATTERING ANGLES (2θ)

Fig.3

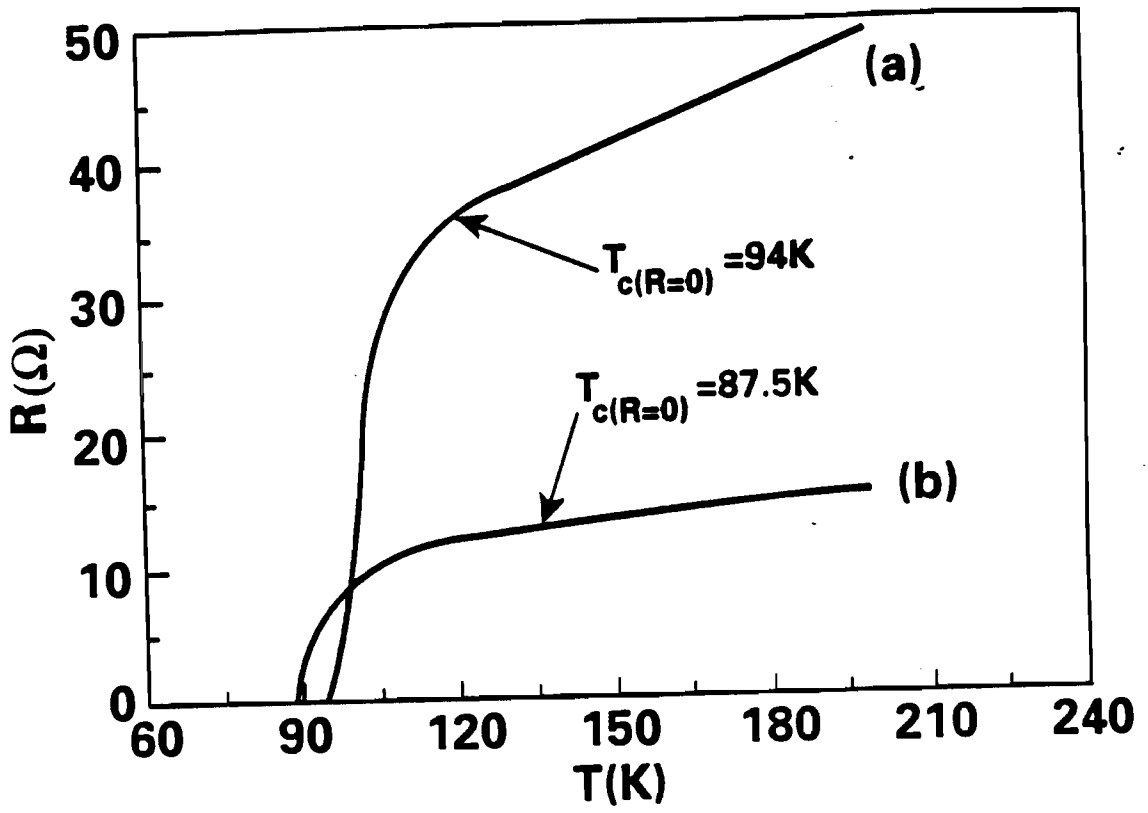

50
40
30
20
10
0
R(Ω)
60
90
120
150
180
210
240
T(K)
(a)
(b)
$T_{c(R=0)}$ =94K
$T_{c(R=0)}$ =87.5K

Fig 4

METALORGANIC CHEMICAL VAPOR DEPOSITION OF HIGHLY TEXTURED SUPERCONDUCTING $YBa_2Cu_3O_{7-x}$ FILMS

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ABSTRACT

C-axis textured single phase superconducting $YBa_2Cu_3O_{7-x}$ films have been successfully grown on the yttria-stabilized zirconia (100) substrates by using the metalorganic chemical vapor deposition technique. After the post annealing the films deposited on the yttria-stabilized zirconia substrates exhibited a highly textured x-ray pattern with c-axis perpendicular to the substrate surface. These films show an onset superconducting transition temperature of 93K with the resistance becoming zero at 84K. The films deposited on sapphire show a semiconducting feature in the normal state with a broad superconducting transition at much lower temperatures (10-40K). In order to gain some insight onto the growth process, we also studied the mass transport of metalorganic compounds as a function of source temperature, flow rate and reactor pressure.

INTRODUCTION

Since the discovery of high T_c superconductivity in the Y-Ba-Cu-O system,[1,2] several deposition techniques have succeeded in making the superconducting $YBa_2Cu_3O_{7-x}$ films with transition temperatures above liquid nitrogen temperature.[3-12] Among the thin film deposition techniques, one of the most important ones is the metalorganic chemical vapor deposition (MOCVD), which is currently the dominant method in depositing device quality III-V and II-VI compounds.[13] The method has the advantage of making the thin films in a low vacuum environment and can easily be scaled to production level. We report here our recent research on high temperature superconducting $YBa_2Cu_3O_{7-x}$ films deposited by MOCVD. The results show that after post-annealing, highly c-axis oriented single phase superconducting $YBa_2Cu_3O_{7-x}$ films can be obtained reproducibly on the yttria stabilized zirconia (YSZ) (100) substrates with T_c (R = 0) at 84K. Under similar processing conditions, the films deposited on sapphire ($1\bar{1}02$) also show a single phase $YBa_2Cu_3O_{7-x}$ structure with a very broad superconducting transition reaching the zero resistance at much lower temperature (10-40K).

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EXPERIMENT

Fig. 1 is a schematic diagram of the MOCVD system used for the deposition of the thin films. Metal β-diketonate complexes of $Y(C_{11}H_{19}O_2)_3$, $Ba(C_{11}H_{19}O_2)_2$ and $Cu(C_{11}H_{19}O_2)_2$ were used as the metalorganic precursors, which will be referred to as $Y(thd)_3$, $Ba(thd)_2$ and $Cu(thd)_2$. Each individual precursor source was placed in a separate stainless steel tube wrapped with heating tapes. An auxiliary outlet was introduced to avoid the deposition from the initial surge and unsteady gas flow. Argon was used as the carrier gas. By carefully controlling the gas flow rates and the source temperatures, the metalorganic precursors were evaporated and carried by argon gas to the reactor after premixing with oxygen gas, which

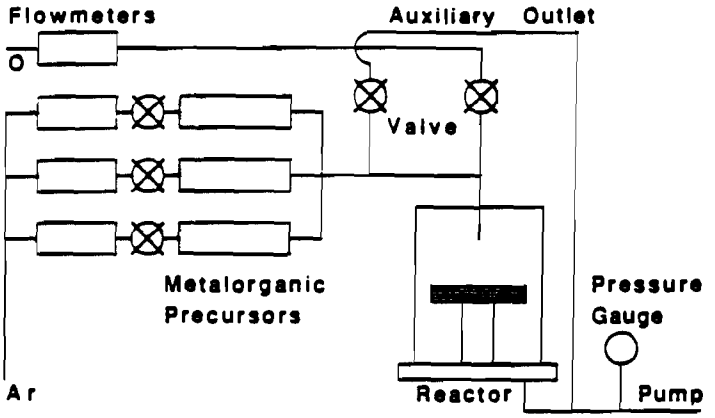

Fig. 1. Schematic diagram of the metalorganic chemical vapor deposition system used for the deposition of the thin films.

was at a flow rate of 1000 sccm. A warm wall vertical reactor made of stainless steel was used with a resistive heating stage for the deposition. The temperature of the susceptor was set at 650°C.

STUDY OF THE DEPOSITION PROCESS

In order to gain some insight into the deposition of $YBa_2Cu_3O_{7-x}$ superconducting films, first we investigated the deposition of Y_2O_3, $BaCO_3$ and CuO films by MOCVD. These films have been successfully deposited on fused quartz substrates. The Y_2O_3 and $BaCO_3$ films deposited on fused quartz substrates were transparent and had shiny surfaces. The CuO films show dark brown color generally with rougher surface under the flow rates and source temperatures investigated. Fig. 2 shows the x-ray diffraction patterns of the Y_2O_3, $BaCO_3$ and CuO thin films obtained from the respective metal β-diketonates when a single component is sent to the reactor at a time. As can be seen, they all show sharp and pronounced diffraction peaks indicating a polycrystalline structure on the quartz substrates.

Fig. 3 shows the mass transport rates as a function of carrier gas flow rates for $Cu(thd)_2$, $Ba(thd)_2$ and $Y(thd)_3$. The pressure was 50 torr on

the sources and in the reactor with the Y and Cu compounds set at 160°C and the Ba compound set at 300°C. These experiments show that the mass transport rates are not very sensitive to the carrier gas flow rates for Y and Ba but for Cu the mass transport increases strongly with increasing flow rate. Above 500 sccm, the mass transport is quite insensitive to a change in the flow rate even for Cu. It should be noted that we need a

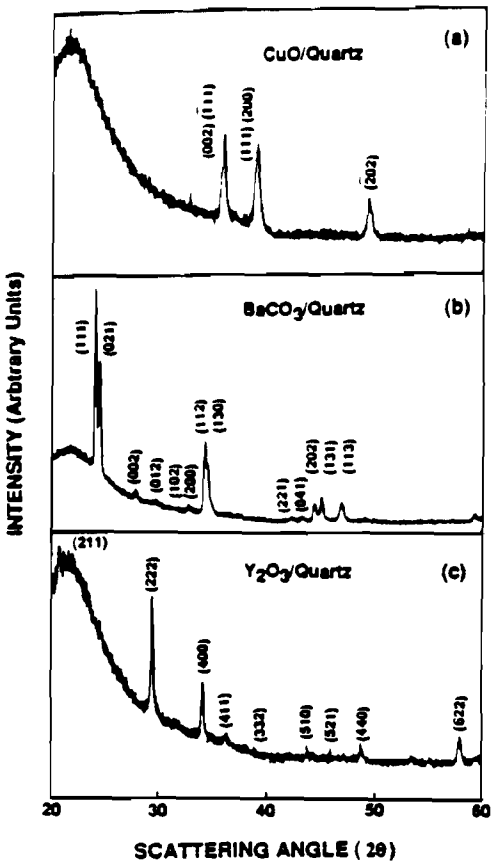

Fig. 2. X-ray diffraction patterns for the films of a) CuO, b) $BaCO_3$ and c) Y_2O_3 deposited on quartz.

temperature for the Ba precursor which is almost double the temperature needed for Cu and Y to obtain a comparable mass transport. Fig. 4 shows the mass transport rates as a function of reactor pressure. Again, we note that the Ba and Y precursors do not vary much in the pressure range studied in comparison to the more rapid variation for Cu. Fig. 5 shows the mass transport rates in the log scale as a function of the inverse source temperature for the Y, Ba and Cu precursor at a reactor pressure of 50 torr. It is clear from the figure that the Cu and Y precursors are much more volatile in comparison to the Ba precursor and the order of the volatility for these three compounds follows the corresponding ionic radius quite well.[14]

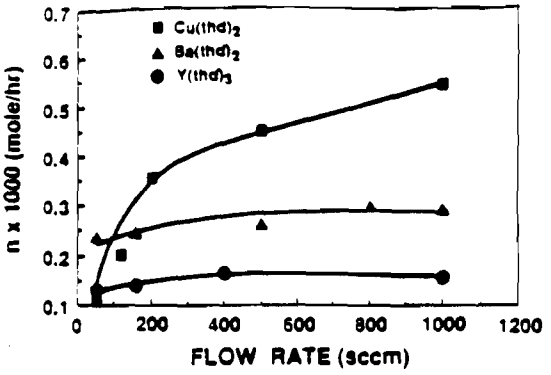

Figure 3. The mass transport rates as a function of carrier gas flow rates for $Cu(thd)_2$, $Ba(thd)_2$ and $Y(thd)_3$. The source temperatures were at 160°C for Y and Cu, and at 300°C for Ba.

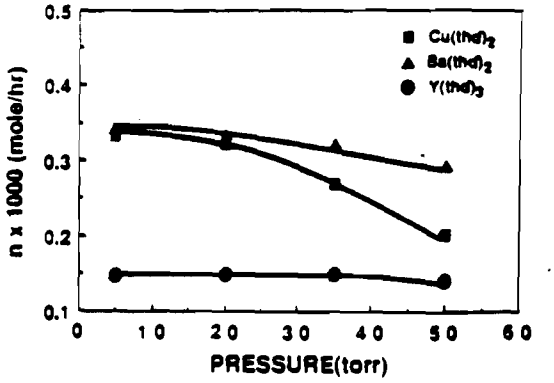

Figure 4. The mass transport rates as a function of the reactor pressure for $Cu(thd)_2$, $Ba(thd)_2$ and $Y(thd)_3$. The source temperatures were at 160°C for Y and Cu, and at 300°C for Ba.

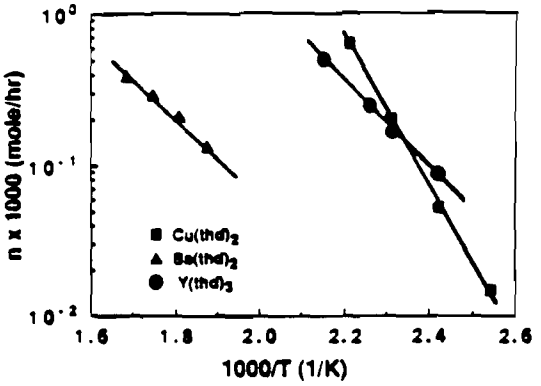

Figure 5. The mass transport rates in the log scale as a function of the inverse source temperature for $Cu(thd)_2$, $Ba(thd)_2$ and $Y(thd)_3$ at a reactor pressure of 50 torr. The flow rates were 125 sccm for Y, 1000 sccm for Ba and 160 sccm for Cu precursors.

The mass transport studies clearly show that among the deposition parameters the control of the source temperature is the most critical because the mass transport rate depends strongly on the source temperature. Based on these preliminary mass transport studies, the source temperatures were set at 160°C, 300°C and 170°C for the Y, Ba and Cu compounds, respectively, to deposit Y-Ba-Cu-O films. The flow rates were 125 sccm for Y, 1000 sccm for Ba and 160 sccm for Cu with the susceptor temperature set at 650°C. The reactor pressure was 50 torr. The partial pressures of the Y, Ba and Cu metalorganic precursors were estimated to be 3, 11 and 10 millitorrs, respectively. After one hour of deposition at a rate of 10 μm/h, the films were cooled to room temperature under oxygen flow. The as-deposited films on both YSZ and sapphire were black and had very high resistances (10-1000 KΩ) compared to the films after post annealing (10 - 500 Ω). The optimum post annealing conditions under oxygen flow were 950°C for 30 minutes for the films deposited on YSZ substrates, and 895°C for 15 minutes for the films deposited on sapphire. After the high temperature anneals the samples were cooled slowly (about 4°C/min) to ambient temperature.

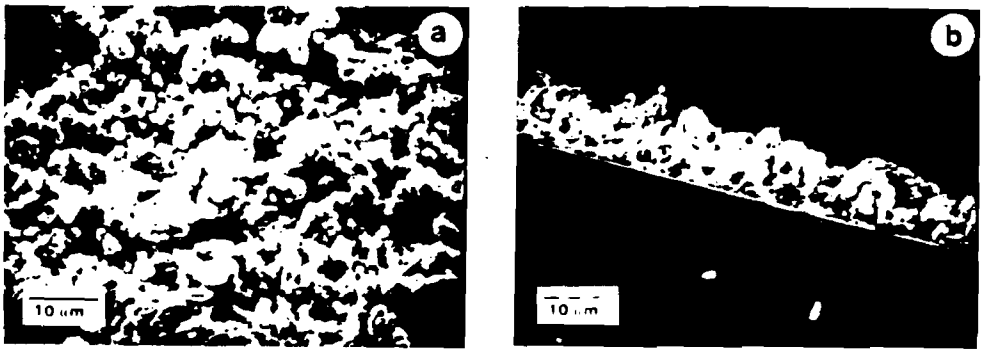

Figure 6. SEM micrographs of (a) the surface and (b) the cross-section for an as-deposited film of YSZ.

The structure of the films was analyzed by using x-ray diffraction and the surface morphology was examined by scanning electron microscopy (SEM). For x-ray diffraction, a digitized horizontal diffractometer from Siemens with Ni-filtered Cu Kα radiation was used. Four-terminal low-frequency ac resistivity measurements were made with indium pressure contacts.

Fig. 6(a) and (b) show surface and cross-section SEM micrographs, respectively, of an as-deposited film on YSZ substrate. As can be seen, the surface is fairly rough and the film consists of an aggregation of micron-size particles. The film seems to be highly porous, possibly due to homogeneous nucleation in the gas phase. Fig. 7(a) and (b) show surface and cross-section SEM micrographs, respectively, of the same film after post annealing at 950°C for 30 minutes. The post annealing greatly improves the surface morphology and eliminates the porosity, providing a dense film. No cracking or peeling was observed in the films examined with thicknesses as high as 10 μm. Similar results were obtained for the films deposited on sapphire ($1\bar{1}02$) substrates.

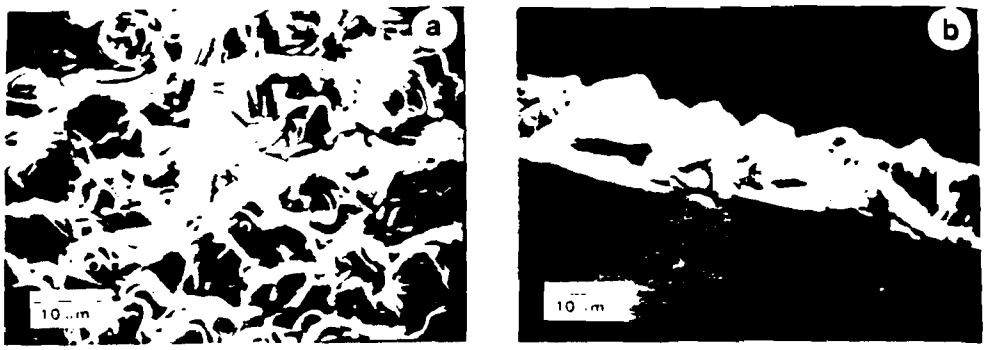

Figure 7. SEM micrographs of (a) the surface and (b) the cross-section for the film deposited on YSZ after post annealing at 950°C for 30 minutes.

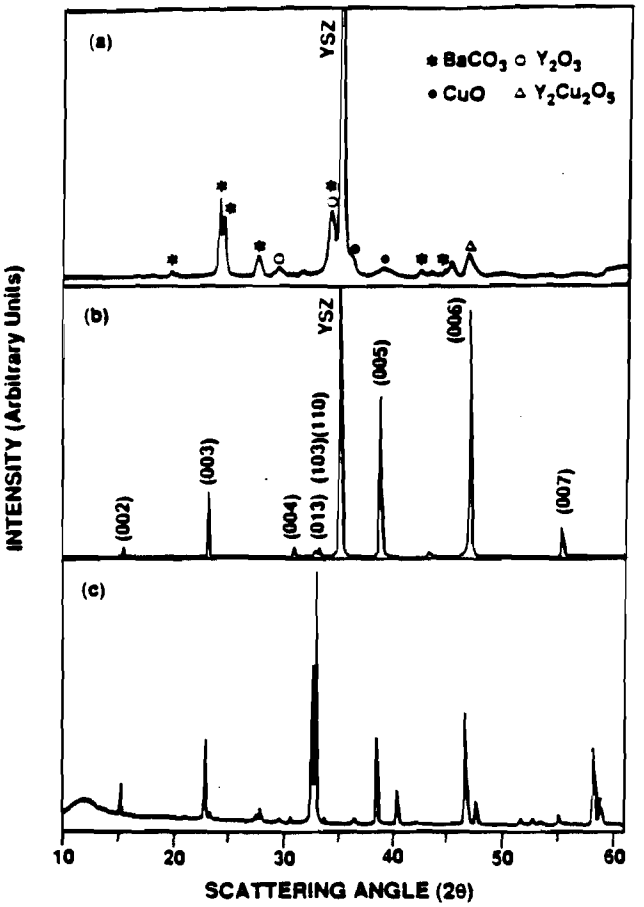

Figure 8. X-ray diffraction patterns for the samples (a) as-deposited on YSZ, (b) post-annealed at 950°C for 30 minutes, and (c) the powdered bulk $YBa_2Cu_3O_{7-x}$ superconductor.

-section for
0°C for 30

The x-ray diffraction pattern of an as-deposited film on YSZ is shown in Fig. 8(a). This pattern shows that the as-deposited film is a mixture of yttrium oxide, copper oxide and barium carbonate and yttrium copper oxide. Electron microprobe analysis provides evidence that the mixture is homogeneous at submicron level. Similar results were obtained for the films deposited on sapphire. In Fig. 8(b), the diffraction pattern shows that, after post annealing, the film on YSZ has a single phase orthorhombic $YBa_2Cu_3O_{7-x}$ structure. This conclusion is drawn by comparing the thin film pattern in Fig. 8(b) to the pattern in Fig. 8(c) obtained from a powdered bulk superconducting $YBa_2Cu_3O_{7-x}$ sample. The pattern for the film shows that all the (00ℓ) lines have very pronounced intensity, indicating a highly textured structure with the c-axis oriented perpendicular to the substrate surface. It is remarkable that films with thicknesses as large as 10 μm can be grown almost completely textured. Highly textured films are important because of the large critical currents they can carry.[3,11] In Fig. 8(b), there are two extra peaks, which cannot be associated with the $YBa_2Cu_3O_{7-x}$ structure. The peak at 35° comes from the YSZ substrate. The peak at 43° can be attributed to $BaZrO_3$ compound forming at the interface due to the reaction between the film and the substrate.[15] Fig. 9 shows the x-ray diffraction pattern of a film deposited on a sapphire ($1\bar{1}02$) after post-annealing at 895°C for 15 minutes. This pattern also shows a well crystallized $YBa_2Cu_3O_{7-x}$ phase in addition to a small amount of CuO.

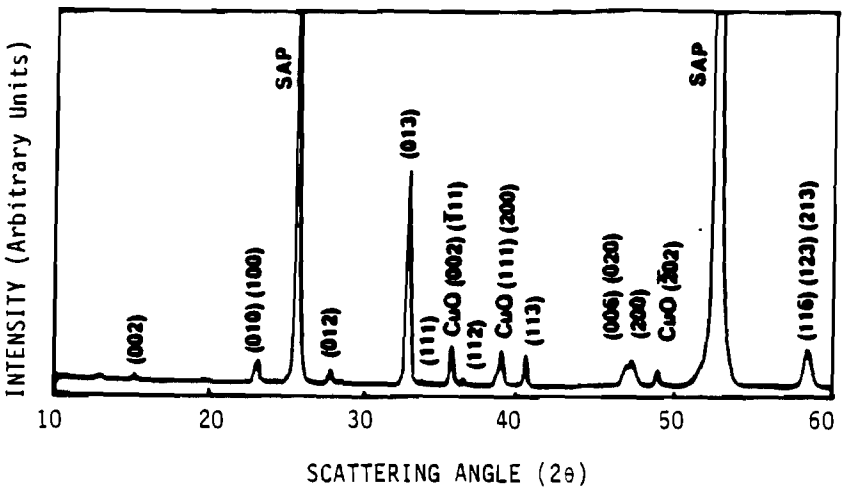

Figure 9. X-ray diffraction pattern of a $YBa_2Cu_3O_{7-x}$ film deposited on a sapphire ($1\bar{1}02$) after post annealing at 895°C for 15 minutes.

eposited on
(c) the

Fig. 10 shows the result of the resistivity measurements as a function of temperature for films deposited on YSZ and sapphire. The contact resistances were 20 Ω and 200 Ω for films on YSZ and sapphire, respectively. The film on YSZ in Fig. 10 shows a sharp transition with an onset of 93 K, zero resistance at 84 K, and a width (10-90%) of 4 K. The resistivities of

the films on YSZ substrates are about 4.5×10^{-4} μΩ-cm at room temperature. The resistivity of the film on YSZ decreases linearly from room temperature down to the transition onset with a resistivity ratio ρ_{300K}/ρ_{95K} of 2.6 indicating good metallic behavior in the normal state. The resistivity of

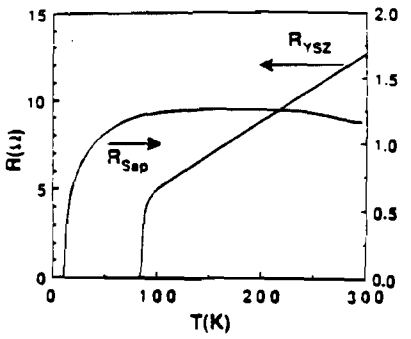

Figure 10. The result of resistivity measurements as a function of temperature for films deposited on YSZ and sapphire.

the film deposited on sapphire exhibits semiconducting behavior in the normal state. This film has a resistance peak value just above the superconducting transition. The zero resistance temperature is as low as 10 K indicating a strong interaction between the sapphire substrate and the film.

In summary, highly textured single phase $YBa_2Cu_3O_{7-x}$ thin films have been obtained by the MOCVD technique on YSZ (100) substrates with thicknesses as large as 10 μm. SEM shows a dense recrystallized homogeneous $YBa_2Cu_3O_{7-x}$ film after post annealing at 950°C for 30 minutes. X-ray diffraction indicates a mixture of metal oxides and carbonates for the as-deposited films and a c-axis highly oriented single phase $YBa_2Cu_3O_{7-x}$ with orthorhombic structure for the post annealed ones. Resistivity measurements show good metallic behavior in the normal state for the film deposited on YSZ with a superconducting onset temperature of 93 K and a zero resistance temperature of 84 K.

ACKNOWLEDGEMENTS

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A Review of Metalorganic Chemical Vapor Deposition of High-Temperature Superconducting Thin Films

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ABSTRACT

A status report is given on the metalorganic chemical vapor deposition (MOCVD) of high-temperature superconducting thin films. The advantages of MOCVD processing manifest themselves in the quality of the films produced, and in the economy of the process. Metalorganic precursor requirements, deposition parameters and film properties are discussed. Also difficulties have been identified in making MOCVD a manufacturing technology. To solve these problems, future research directions are proposed.

1. INTRODUCTION

The recent discovery of some oxide superconducting materials with transition temperatures above 77 K represent a major breakthrough for both science and technology.[1,2] But before these materials fulfill their promises, some processing techniques need to be developed to prepare these materials in the required shapes and sizes with high critical currents and high critical fields. These oxide superconducting materials are brittle and the physical properties are very process dependent. The brittleness issue can be addressed by using these materials in the form of either coatings or composites. The physical properties of these materials can be best controlled during the deposition by using a technique which allows the control of most of the thermodynamic variables during the growth. The metal-organic chemical vapor deposition (MOCVD) technique is such a technique.[3] This technique is currently the most important technique in the deposition of the compound thin films for electronics and optical device applications.

The advantages of MOCVD processing manifest themselves in the quality of the films produced, and in the economy of the process. Film characteristics such as conformal coverage and high purity, and processing benefits such as low temperature and radiation-damage free deposition, deposition selectivity and film stress and grain size control allow one to make unique, high quality films. At the same time, the high throughput and low cost per wafer associated with MOCVD processing make it very attractive economically.

In this paper, we review the status of the preparation of the high-temperature superconducting thin films by the MOCVD technique, and suggest future research directions for improvement.

2. DESCRIPTION OF THE MOCVD TECHNIQUE

In this growth process, one or more of the film constituents are transported to the reaction zone in the form of metalorganic compounds. The formation of the desired compound occurs via the pyrolysis of the metalorganics and the subsequent recombination of the atomic or molecular species at or near the heated substrate. The basic simplicity of the reaction and the gaseous nature of the reactants have established MOCVD as a useful epitaxial technology. The process can be well controlled by fixing the flow rates and thus the partial pressure of the various reactants with electronic mass flow controllers. Similarly, complex multilayer epitaxial structures are readily formed by exchanging one gas composition for another using automated gas-mixing systems. The pyrolytic nature of the reaction requires that only the substrates be heated to ensure efficient deposition, thus simplifying the temperature control.

Fig. 1 is a schematic diagram of the MOCVD system used for the deposition of the $YBa_2Cu_3O_{7-x}$ thin films.[4] The 2,2,6,6-tetramethyl-3,5-heptanedione (thd) compounds of Y, Ba, and Cu were used as the metalorganic precursors, which will be referred to as $Y(thd)_3$, $Ba(thd)_2$ and $Cu(thd)_2$. Each individual precursor source was placed in a separate stainless steel tube wrapped with heating tapes. An auxiliary outlet was introduced to avoid the deposition from the initial surge and unsteady gas flow. Argon was used as the carrier gas. By carefully controlling the gas flow rates and the source temperatures, the metalorganic precursors were evaporated and carried by argon gas to the reactor after premixing with oxygen gas. A warm-wall vertical reactor made of stainless steel was used with a resistive heating stage for the deposition.

3. MOCVD PRECURSORS

The nature of metalorganic compounds used to transport metals onto the surface of the substrate determines both the growth conditions and the properties of the films grown. A suitable precursor should have high enough vapor pressure for vapor transport; should not decompose at the operating temperatures losing its volatility; should be stable at room temperature for long term storage. For the deposition of superconducting oxide films, finding precursors satisfying the requirements above presents a challenge. So far, metal β-diketonates[5] have been used in the deposition of high-temperature superconducting films. These compounds are easy to handle because of their air-stability. However, they need to be heated to several hundred degrees centigrade to get high enough vapor pressure for transport, and they decompose at the precursor operating temperatures over an extended period. Other promising classes of compounds are some alkyl substituted cyclopentodienyl compounds developed at Georgia Tech. These compounds are liquid at room temperature and have much higher vapor pressures. Table I shows a list of metalorganic compounds which might be useful in the deposition of superconducting thin films.

4. MASS TRANSPORT STUDIES

Mass transport studies are important in the establishment of the MOCVD process parameters. Fig. 2 shows the mass transport rates as a function of carrier gas flow rates for $Cu(thd)_2$, $Ba(thd)_2$ and $Y(thd)_3$. The pressure was 50 torr on the sources and in the reactor with the Y and Cu compounds set at 160°C and the Ba compound set at 300°C. These experiments show that the mass transport rates are not very sensitive to the carrier gas flow rates for Y and Ba, but for Cu the mass transport increases strongly with increasing flow rate. Above 500 sccm, the mass transport is quite insensitive to a change in the flow rate even for Cu. It should be noted that we need a temperature for the Ba precursor which is almost double the temperature needed for Cu and Y to obtain a comparable mass transport. Fig. 3 shows the mass transport rates as a function of reactor pressure. Again, we note that the Ba and Y precursors do not vary much in the pressure range studied in comparison to the more rapid variation for Cu. Fig. 4 shows the mass transport rates in the log scale as a function of the inverse source temperature for the Y, Ba and Cu precursor at a reactor pressure of 50 torr. It is clear from the figure that the Cu and Y precursors are much more volatile in comparison to the Ba precursor and the order of this volatility for these three compounds follows the corresponding ionic radius quite well.[5]

In order to understand the deposition process further, we have carried out a systematic study of the mass transport for the precursors as a function of the deposition time. The results are shown in Fig. 5 (a) and (b). These experiments were performed with fixed conditions as follows, the reactor temperature at 600°C, pressure at 50 torr, gas flow rates at 500 sccm for Tl, Ba and at 85 sccm for Cu, Ca precursors. The metalorganic source temperatures were at 165, 160, 255 and 285°C for Tl, Cu, Ca and Ba precursors, respectively. All 4 components were run simultaneously. The starting chemical weights were at 0.5 grams for Cu and Ba, 0.6 grams for Tl and 0.4 grams for Ca, respectively. The transport time was started after the stabilization of the initial surge and unsteady gas flow. This should explain the zero offset in the figures. As can be seen, under deposition condition specified, the Cu and Ca precursors exhibit a linear behavior throughout the one-hour deposition time, while the data for Tl and Ba show a saturation after about 30 minutes. When the starting chemical weights are doubled, we have a linear behavior also for Tl and Ba as shown in Fig. 6(a) and (b). This suggests that in the first case most of the usable precursors were consumed within the first 30 minutes and the residue is just some involatile compound. These observations are consistent with the observation by Yamane et al.[6] that at a fixed evaporation temperature these compounds evaporate at a constant rate for the duration of several hours.

5. SUPERCONDUCTING THIN FILMS DEPOSITED BY MOCVD

The MOCVD technique has been used in the deposition of Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O and Tl-Ca-Ba-Cu-O thin films. Next, the results obtained so far for each class of compound will be reviewed.

5.1 Y-Ba-Cu-O films

Thin films of the $YBa_2Cu_3O_{7-x}$ compound have been deposited by using MOCVD by several research groups world-wide.[4,7-18] In the majority of the studies, $Y(thd)_3$, $Ba(thd)_2$ and $Cu(thd)_2$ were used as the precursors. In few cases, fluorine-substituted β-diketonates have been used as the precursor, since they have higher vapor pressures.[14-16] However, these compounds require higher deposition temperatures in the presence of H_2O vapor to eliminate fluorine incorporation into the film. The superconducting thin films were obtained either by in-situ deposition, or by depositing the film at low temperatures (400-650°C) and by subsequent post-annealing in the temperature range 900-950°C. Fig. 7 shows the resistance as a function temperature for a film deposited at 650°C on yttria-stabilized zirconia (YSZ) and then post-annealed at 950°C under oxygen flow.[13] Growth rate was about 10 μm/hr and the film was c-axis oriented.

The in-situ deposition process uses lower deposition temperatures and produces very high quality c-axis oriented films. Deposition at low temperatures is important because it lowers the interdiffusion between the film and the substrate. The typical conditions for the in-situ deposition of $YBa_2Cu_3O_{7-x}$ is given in Table II. One of the most exciting things about the MOCVD technique is the very high critical current densities observed in the films grown by this technique.[17,19] The value of J_c is 4.1×10^5, 1.9×10^5, and 6.5×10^4 A/cm^2 at 2, 10, and 27 T, respectively.[19] Fig. 8 shows critical currents of a MOCVD grown film at 77.3 K and in magnetic fields up to 27 T.

5.2 Bi-Sr-Ca-Cu-O Films

Bi-Sr-Ca-Cu-O (BSCCO) films were prepared on MgO (100) single-crystal substrates by MOCVD using β-diketone compounds of Sr, Ca and Cu and Bismuth triethoxide or triphenylbismuth.[20-22] Table II gives the typical growth conditions for the growth of BSCCO. The films were c-axis oriented and the growth rates were in the range of 2-3 μm/h. The major phase was the $Bi_2(Sr,Ca)_3Cu_2O_x$, T_c = 85 K with some incorporation of the $Bi_2(Sr,Ca)_4Cu_3O_x$, T_c = 110 K phase. Four-point-probe measurements reveal the onset of film superconductivity at ~ 110 K and zero resistance at ~ 75 K. The SEM micrographs of the surface and cross section of the annealed films show flat and mica-like flakes overlapping.

5.3 Tl-Ca-Ba-Cu-O Films

The Tl-Ca-Ba-Cu-O film growth presents a challenge to the thin-film growers because of the high vapor pressure of Tl over the superconducting compounds. Since the MOCVD technique does not require a high vacuum, the volatility of thallium may be used as an advantage for the in-situ preparation of the Tl-based superconducting thin films. So far, however, the Tl-Ca-Ba-Cu-O thin films are obtained in the two steps. First the Ca-Ba-Cu-O films have been deposited at

600°C by using the β-diketone compounds of Ca, Ba, and Cu. Then, Tl-O is introduced in a sealed crucible at 800°C to achieve the superconducting phase.[23,24] Superconducting $Tl_2CaBa_2Cu_2O_x$ thin films have been successfully grown on the single crystal sapphire ($1\bar{1}02$) substrate by using the MOCVD technique without any intermediate buffer layer.[23] Fig. 9 shows the result of resistivity measurements as a function of temperature for a film deposited on sapphire ($1\bar{1}02$). Superconducting transition temperatures have been obtained with zero resistance at 94 K and 100 K for sapphire[23] and YSZ[24] substrates, respectively.

6. CONCLUSIONS

The MOCVD technique has been used to deposit $YBa_2Cu_3O_{7-x}$, Bi-Sr-Ca-Cu-O and Tl-Ca-Ba-Cu-O thin films with qualities comparable to those prepared by using the other techniques. Particularly, the critical currents under high magnetic fields in the $YBa_2Cu_3O_{7-x}$ films prepared by MOCVD are among the largest ever observed in oxide superconductors. However, at the present time, it is not clear whether MOCVD will be the technique for the production of oxide superconductors in large scale. This will depend largely on the development of new precursors with more volatility and stability, and the realization of in-situ deposition below 650°C. A systematic study is required to improve the β-diketonates known and to discover new classes of compounds. The plasma assisted MOCVD may be used to bring the deposition temperature below 650°C. Also, directed energy sources, such as lasers, may be used for depositing superconducting thin films selectively within the MOCVD reactor.

7. ACKNOWLEDGEMENTS

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Table I Some Metalorganic Compounds for the Deposition of Superconducting Thin Films by MOCVD (superscripts are reference numbers)

Compound	Melting Point(°C)	Vapor Pressure (mmHg)	Physical/Chemical Characteristics
$Ba(thd)_2$	172 [25,27]	0.8 (220°C)	White cry. needles in EtOH, difficult to crystallize.
$Ca(thd)_2$	224 [25,27]	1.1 (160°C)	White cry. needles in EtOH, difficult to crystallize.
$Cu(thd)_2$	201	0.5 (135°C)	Blue to purple cubic cry. in EtOH, ether, hexane, toluene.
$Sr(thd)_2$	200 [25,27]		White cry. needles in EtOH or ether.
Tl(thd)	240	14.4 (165°C)	Light-yellow needles in EtOH or ether.
$Y(thd)_3$	168 [26]	0.2 (135°C)	White cry. in EtOH.
$La(Cp)_3$	395 [28]	1.4 (100°C)[29]	White cry. A.S.
$La(MeCp)_3$	155 [28]		White cry. A.S.
$La(isopropylCp)_3$	< RT	1.5 (100°C)[29]	Light-yellow viscous liquid, A.S. dis. 170-220°C, 10 torr.
$CpCuP(Et)_3$	127 [30]		White cry. needles, sub. 60°C , 5 torr.
$(EtCp)CuP(Et)_3$	< RT	3-4 (110-120°C)	Light-yellow/purple liquid, A.S.
$Y(Cp)_3$	295 [28]	0.002 (100°C)[31]	Pale yellow cry. A.S.
$Y(isopropylCp)_3$	< 45		Light-yellow solid A.S. above RT, dis. 170-190°C,10 torr.
$Cu(fod)_2$	68	0.4 (100°C)[5]	Blue-green solid.
$Ba(fod)_2$	162		Yellow-white solid, dis. 200-220°C,5 torr.
$Y(fod)_3$	108 [32]		Yellow-white solid dis. 200-220°C,5 torr.

thd=$C_{11}H_{19}O_2$, Cp=C_5H_5, MeCp=C_6H_7,
isopropylCp=C_8H_{11}, Et=C_2H_5, fod=$C_{10}H_{10}O_2F_7$.
dis.=distill, sub.=sublime, A.S.=air sensitive, cry.=crystal,
EtOH=ethanol, RT=room temperature.

Table II. MOCVD Deposition Conditions [6]

	YBCO	BSCCO
Vaporizer Temperature	$Y(thd)_3$: 110-130°C $Ba(thd)_2$: 240-260°C $Cu(thd)_2$: 110-130°C	$Bi(C_2H_5O)_3$: 130-140°C $Sr(thd)_2$: 220-230°C $Ca(thd)_2$: 180-190°C $Cu(thd)_2$: 110-120°C
Deposition Temperature	800-900°C	770°C
Total Gas Pressure	10 Torr	1 Torr
Carrier Gas (Ar) Flow Rate	200 ml/min	200 ml/min
O_2 Gas Flow Rate	100 ml/min	100 ml/min
Deposition Time	1 hr	1 hr

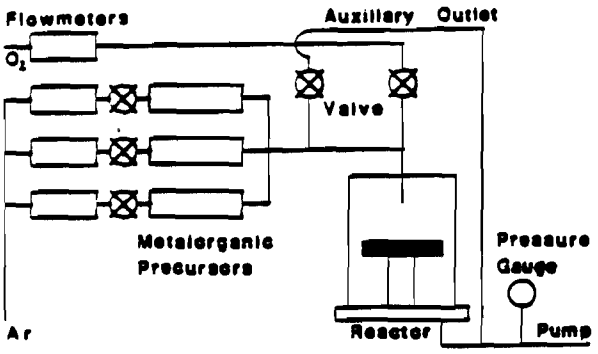


Figure 1. Schematic diagram of the metalorganic chemical vapor deposition system.[4]

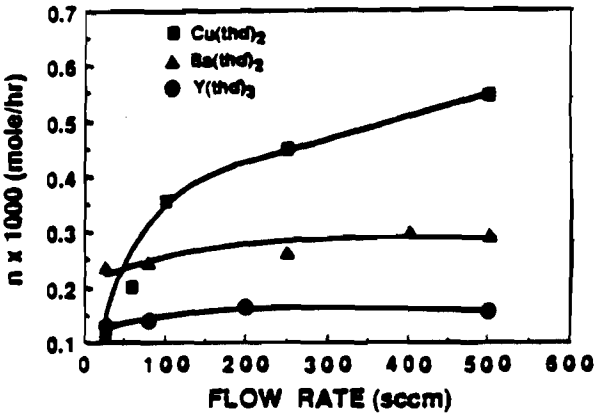


Figure 2. The mass transport rates as a function of carrier gas flow rates for various precursors with source temperature at 160°C for Y and Cu, 300°C for Ba.[4]

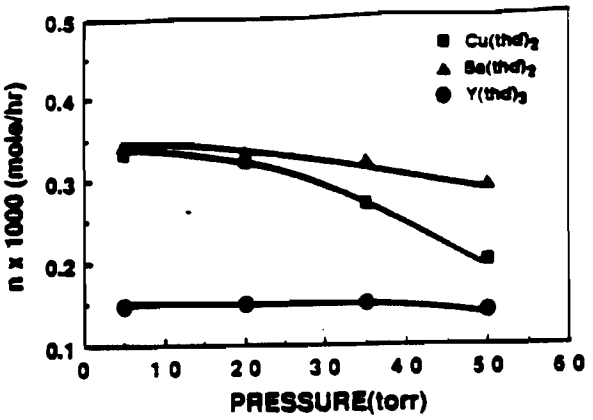


Figure 3. The mass transport rates as a function of the reactor pressure for various precursors with source temperature at 160°C for Y and Cu, 300°C for Ba.[4]

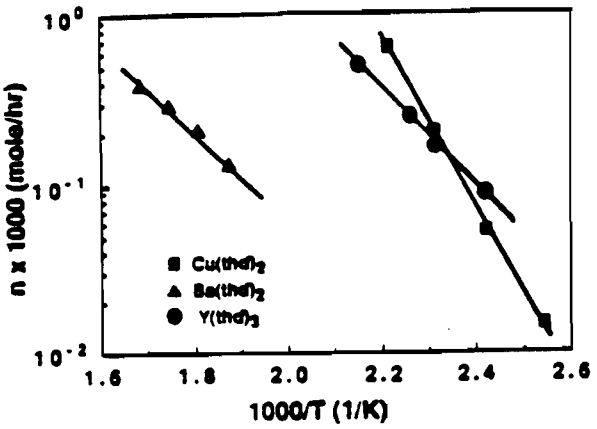
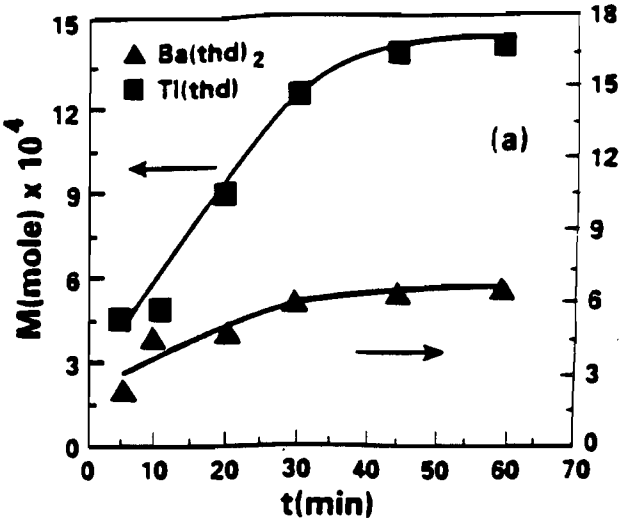


Figure 4. The mass transport rates as a function of the inverse source temperature for various precursors with reactor pressure at 50 torr, gas flow rates at 125 sccm for Y, 1000 sccm for Ba and 160 sccm for Cu.[4]



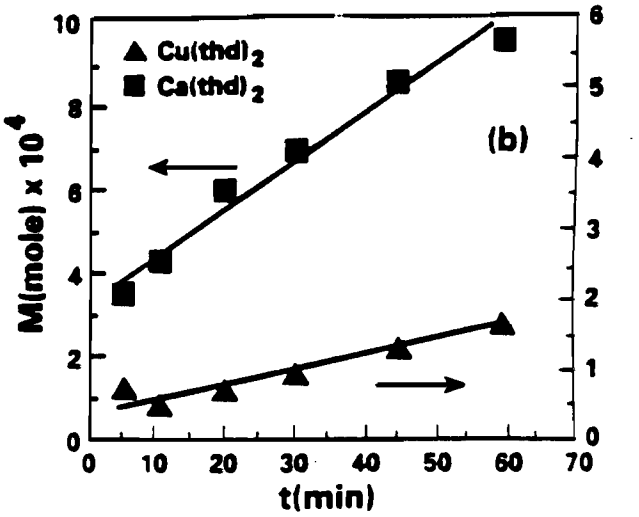


Figure 5. The mass transport as a function of deposition time for the metal precurcors of (a) Ba, Tl and (b) Cu, Ca with starting weights at 0.5 g for Cu, Ba, 0.6 g for Tl and 0.4 g for Ca.[23]

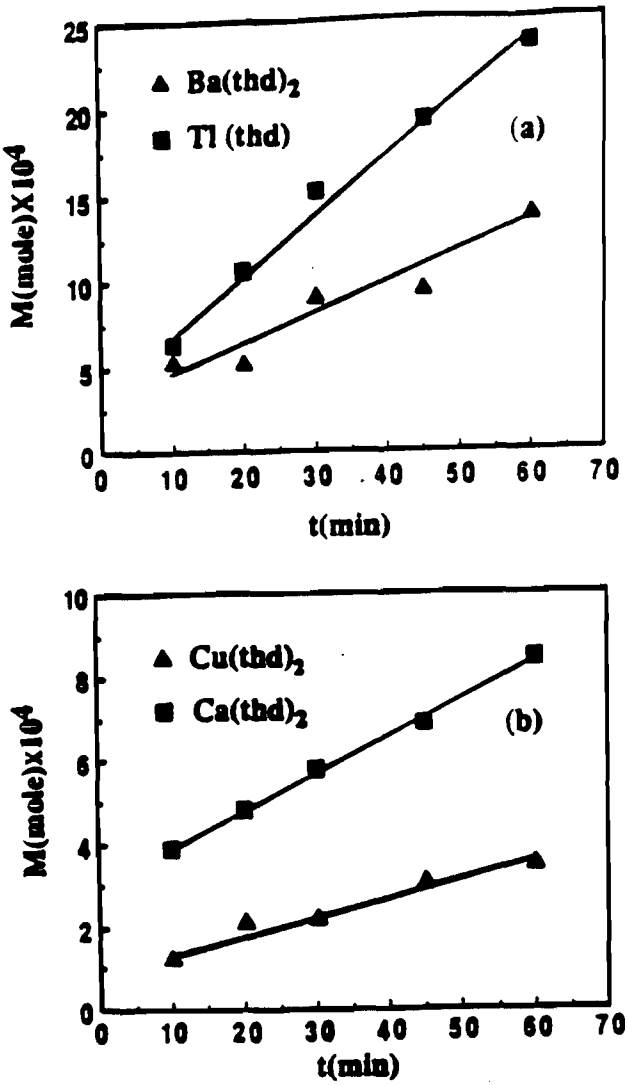


Figure 6. The mass transport as a function of deposition time for the metal precursors of (a) Ba, Tl and (b) Cu, Ca with starting weights at 1.0 g for Cu, Ba, 1.2 g for Tl and 0.8 g for Ca.

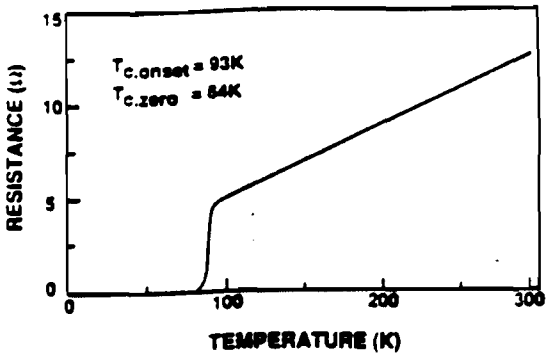


Figure 7. Resistance as a function of temperature for a post-annealed $YBa_2Cu_3O_{7-x}$ film deposited on YSZ.[13]

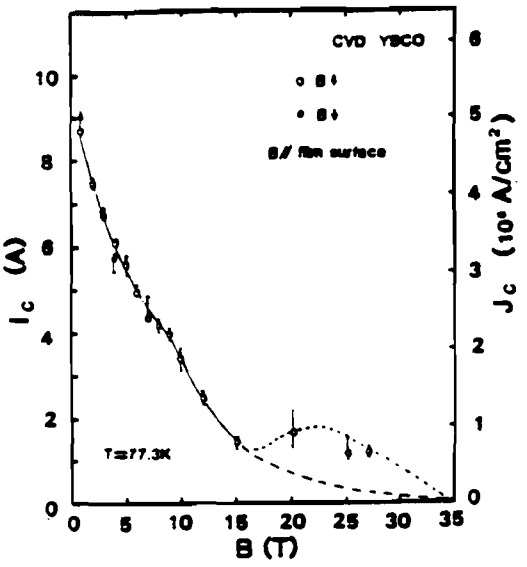


Figure 8. Magnetic field dependence of critical currents at 77.3 K up to 27 T for the thin film deposited by MOCVD technique.[19]

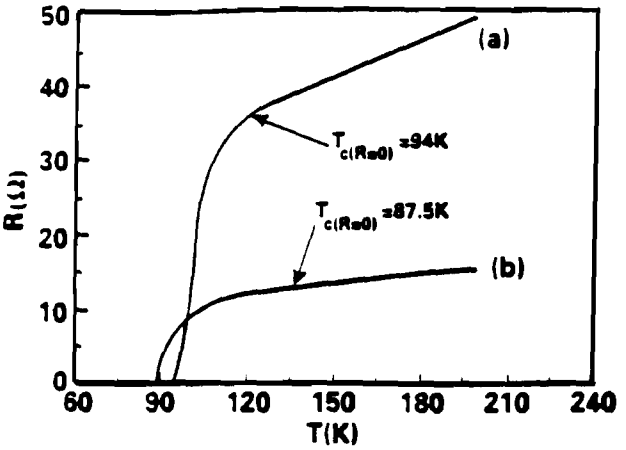


Figure 9. Resistance as a function of temperature for a $Tl_2CaBa_2Cu_2O_y$ thin film on sapphire post-annealed at 850°C in air for 40 min (b), and followed by further treatment at 500°C in O_2 for 6 hours (a).[23]

Erb:l

MeV Ion Channeling Studies of [111] CdTe Films on [111] GaAs Substrates.

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Abstract

Group II-VI compound semiconductors such as CdTe can be epitaxially grown on III-V materials (e.g. GaAs). These films possess better physical properties than their bulkgrown counterparts. The present work explores the [111] CdTe/[111] GaAs system by means of MeV ion channeling. It is found that the epitaxy is quite good (backscatter minimum yields of 15%) for thickness greater than 100Å, which is remarkable considering the 14% lattice mismatch between film and substrate. A narrowing of the Cd angular scan suggests a Cd atom displacement in the lattice. A model based on a Te vacancy is presented to describe the data.

INTRODUCTION:

Present II-VI compound semiconductor device technology is limited by the difficulty of obtaining high quality material from bulk-grown crystals. The combination of high defect and impurity levels restrict the use of these highly useful materials (wide bandgap range) to narrow areas of application due to their resulting poor electronic properties. This problem is being solved to some extent by the epitaxial growth of thin II-VI semiconductor films on III-V semiconductor substrates such as GaAs. Using this approach, the impurity and defect problems in the bulk materials are traded off for the smaller problem of interfacial lattice strain in the epitaxial systems. The strain problem can actually be an advantage when strain levels are tailored to enhance desired electronic properties[1]. This can only be accomplished with an understanding of the type and magnitude of strain present. The following is a description of lattice mismatch induced effects at the CdTe/GaAs interface of CdTe thin films grown on GaAs by metalorganic chemical vapor deposition (MOCVD).

Experiment:

The samples were grown at the Georgia Institute of Technology using a commercial MOCVD System (Cambridge Instruments MR102) with a horizontal reactor. Dimethylcadmium (DMCd) and diisopropyltelluride (DITe) were used as the Cd and Te sources, respectively. The DMCd partial pressure was 136 mTorr. Ultrahigh purity H_2 was used as the carrier gas. The reactor pressure for the growth was 250 Torr. The substrate temperature was kept at 350^0C. A series of CdTe films of thicknesses ranging from 475 Å to 3μm were grown on [111] oriented GaAs substrates at a growth rate of 3.7 μm/h by varying the growth duration. X-ray (2 θ scan) diffraction measurements showed the films to be completely single phase material, oriented with the [111] axis normal to the surface. RBS and ion channeling measurements were made to determine the level of crystallinity. This was accomplished by a comparison of the RBS yield when the sample is aligned with a major symmetry axis parallel to the incoming He^+ beam, to the RBS yield from the random (unaligned) backscattered yield. Angular scans, about the major axes, of the backscattered intensity measured as a function of depth and mass can be used to determine lattice properties such as atom positions and lattice strain[2] .

RESULTS AND DISCUSSION: Fig.1 shows channeling spectra plotted for several thicknesses. It can be seen from this that the surface minimum yield is nearly the same for all thicknesses plotted (15-20%). The yield for the 475Å film is measurably worse than for thicker films possibly indicating some strain, however, the "critical" thickness phenomena would not apply here as the mismatch is far too great[3]. Another observation to be made is that the rate of dechanneling vs. depth is constant as a function of thickness. This shows that most of the dechanneling occurs near the surface (<500A in depth) from the interface. When the crystal is aligned along the off-normal [112] axis the χ_{min} becomes worse by a factor of 2. This indicates that the dislocations and strain present is aligned parallel to the [111] growth direction. The minimum yield for the [112] axis should actually be 40% lower than for the [111] axis, according to calculations. The angular scan shown in Fig. 2 gives the ion channeling flux distributions around the [111] axis for the Cd and Te atoms, as well the GaAs. For each plot the angular minimums are coaxial, however it should be noted that the Cd scan is narrower than the others. This narrowing and accompanying rise in the minimum yield is a result of a small displacement of Cd atoms in the film. It is interesting to note that this is not the case for the Te atoms which show a $\psi_{1/2}$ (angular width) which is close to that of the GaAs substrate. The calculated $\psi_{1/2}$ is slightly larger for Te than measured (1.0^0 vs $.93^0$). It was also observed that the angular scan at the interface is essentially the same as that of the surface indicating that the lattice location and atomic order is unchanged through the entire depth of the film. Angular scans were made around the [112] axis to further study the question of lattice location of the Cd atom (fig. 3). Care was taken to avoid planar channeling around the axis. Fig. 3 shows the Cd width is narrowest, as in the [111] case, indicating the lattice displacement of some of the Cd atoms. The most striking feature of this scan is the $.14^0$ offset of the Cd minimum with respect to the Te and GaAs scans. This condition was found to exist for both the interface region and the surface. Clearly this cannot be accounted for by a tilt in the film growth axis since the Te yield remains coaxial with the GaAs minimum. To explain this by some form of lattice distortion or strain one should see a symmetric offset in the position of the Te minimum as well. The source of this Cd offset must then be related to a condition of the Cd sub-lattice itself. It should be noted that the maximum allowable film thickness to be measured, where the RBS peaks remain well separated

at an energy of 4 MeV, is approximately 1000Å. The measurement shown in Fig. 3 was reproduced several times and was also done on thinner films (475Å) as well. Each measurement yields the same result regardless of which of the "[211]" (e.g. 121,112) axes were measured. The offset was consistently found to be $.14^0 \pm .02^0$ and was always shifted towards the [111] surface normal axis. Ponce[4] et al, has studied the 100 CdTe/100 GaAs system, which bears many similarities to the present case. Their TEM cross-sections indicate a periodic edge dislocation (every 31 Å) which correspond to the 14.6% lattice mismatch where it is shown that for every 7 atomic spacings of CdTe an extra plane of GaAs is jammed into the interface. The lattice mismatch is too large to accommodate the formation of pseudomorphic strained layers at the interface. Our data is consistent with this in that the majority of defects in the film occur within the first 475Å (or less as indicated by channeling) and the Te atoms at the interface remain coaxial with the GaAs atomic rows when scanned around an off-normal axis. Nevertheless the behavior of the Cd angular minimum offset remains to be understood. From the view of purely geometrical considerations this could be accomplished by introducing Te vacancies into the lattice thereby causing the surrounding tetragonally bonded Cd atoms to relax away from the vacant Te lattice site towards a flat trigonal bond configuration with the three remaining Te atoms associated with each of them. This is shown schematically in fig. 4 where it can be seen that the 4 Cd atoms associated with the vacancy protrude into the [112] channel. The distance of protrusion into the channel would depend on the degree of "flatness" of the trigonal bonding configuration. This idea was first applied to relaxation of GaAs surfaces with dangling bonds[5]. The degree of relaxation would depend on next nearest Te neighbor attraction and other lattice effects.

Qualitatively the basic features of the data described above can be satisfied by this vacancy model as given in the following. When a zincblende structure is viewed along the [111] direction, 3 of the 4 tetragonal bonds extend symmetrically outward from the [111] direction with the fourth bond being parallel to this direction. The results shown in fig. 2 could be approximated by assuming these four lattice sites to be Cd atoms and displacing them outward along the bond directions. When the crystal is tilted 19.5 degrees from normal and viewed along the [112] axis, the symmetry is two-fold

and the four displaced atoms are distributed with three of them protruding to the left into a [112] channel and the fourth atom displaced to the right into the narrow [112] channel. The displacements can be reversed, i.e. 3 to the right and one to the left, if the polarity of the film (Cd and Te stacking order) is reversed (See fig. 4). A consequence of this is that the polarity of the film is determined by the sign of the offset of the minimum of the Cd scan, i.e. a Cd minimum shift to a lower angle indicates Te atoms going down first on the GaAs substrate.

To quantitatively fit the angular scans a knowledge of the number of possible vacancies or the actual length is required. Since neither of these parameters can be independently measured by these methods, and also since this Te vacancy concept has been invoked for a geometrical structure argument only , a semi-empirical fit must be made based on a range of possible lattice displacement limits for the Cd atoms calculated from the lattice parameters. When a calculation of the atomic and planar spacing is made using the 6.428Å CdTe lattice constant it can be shown that the maximum allowable displacement (flat trigonal bonding configuration) of a nearest neighbor Cd atom from a Te vacancy is .93Å. This distance is equivalent to the small spacing between the planes as shown in fig. 4. For this displacement the net normal protrusion into the [112] channel is .31Å. However, it is not likely that a full relaxation would occur due to the effects of the next nearest neighbor Te atoms.

Along the [111] direction the normal component of the relaxation extends .87Å into the [111] channel for the 3 radially symmetric Cd atoms surrounding the Te vacancy. A semi-empirical calculation can be done based (somewhat arbitrarily) on an RMS value of the above calculated protrusion (i.e..7(.87)) into the [111] Cd channel and on the measured values of angular width for the Cd and Te channels (where the width of the Te channel is assumed to be equal to the width of an unperturbed Cd channel). Using equations from ref. 6 and the measured values of ψ_{Cd} ($.67^0$) and ψ_{Te}($.92^0$) and assuming a value for $\rho = .1$Å (thermal oscillation) the value for r_x (the displacement distance from the atomic row) is .14 Å. From this value and the calculated RMS value of relaxation we can calculate a value for the Te vacancy density. Knowing that the backscattered intensity falls off as $1/r^2$ as the atomic row is approached and using the total volume density of Cd

atoms divided by three (3 displaced Cd atoms/Te vacancy), we find a 1.7% Te vacancy level is required to obtain the angular widths measured.

The explanation for the apparent shift in the Cd minimum as measured along the [112] is that it is merely an offset due to the asymmetric distribution of protruding Cd atoms (See fig. 5) resulting in an asymmetric backscatter yield from the two dissimilar walls of the channel which when joined together result in an offset minimum.

CONCLUSION:

We have shown that in spite of a rather large lattice mismatch films of [111] oriented CdTe can be epitaxially grown on [111] oriented GaAs and that the mismatch results in defects in the interface region in addition to strain produced by epitaxial growth. It has also been observed that there is a disturbance in the Cd sublattice as evidenced by displaced Cd atoms protruding into the [211] channels in an assymetric manner causing an apparent offset in the Cd angular yield minimum. A model was proposed based on Te vacancy density of 1.7% as a possible explanation for the Cd behavior.

Acknowledgements:

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Figure Captions

Fig. 1 4 Mev He^{++} ion channeling spectra for a series of CdTe film thickness grown on [111] GaAs. Alignment is along the [111] axis.

Fig. 2 Backscattered yield vs. angle for 4 MeV ions channeled along or near the [111] axis of a 900Å thick CdTe film. Individual spectra are plotted for the Cd and Te yield in the film and for the GaAs yield just below the interface.

Fig. 3 Backscattered yield vs. angle for 4 MeV ions channeled along or near the [112] axis of a 900Å thick CdTe film. Individual spectra are plotted for the Cd and Te yield in this film, and for the GaAs yield just below the interface.

Fig. 4 Film cross-section as viewed in the (110) plane. The Cd atoms surrounding the Te vacancy are seen to protrude into the [112] channel.

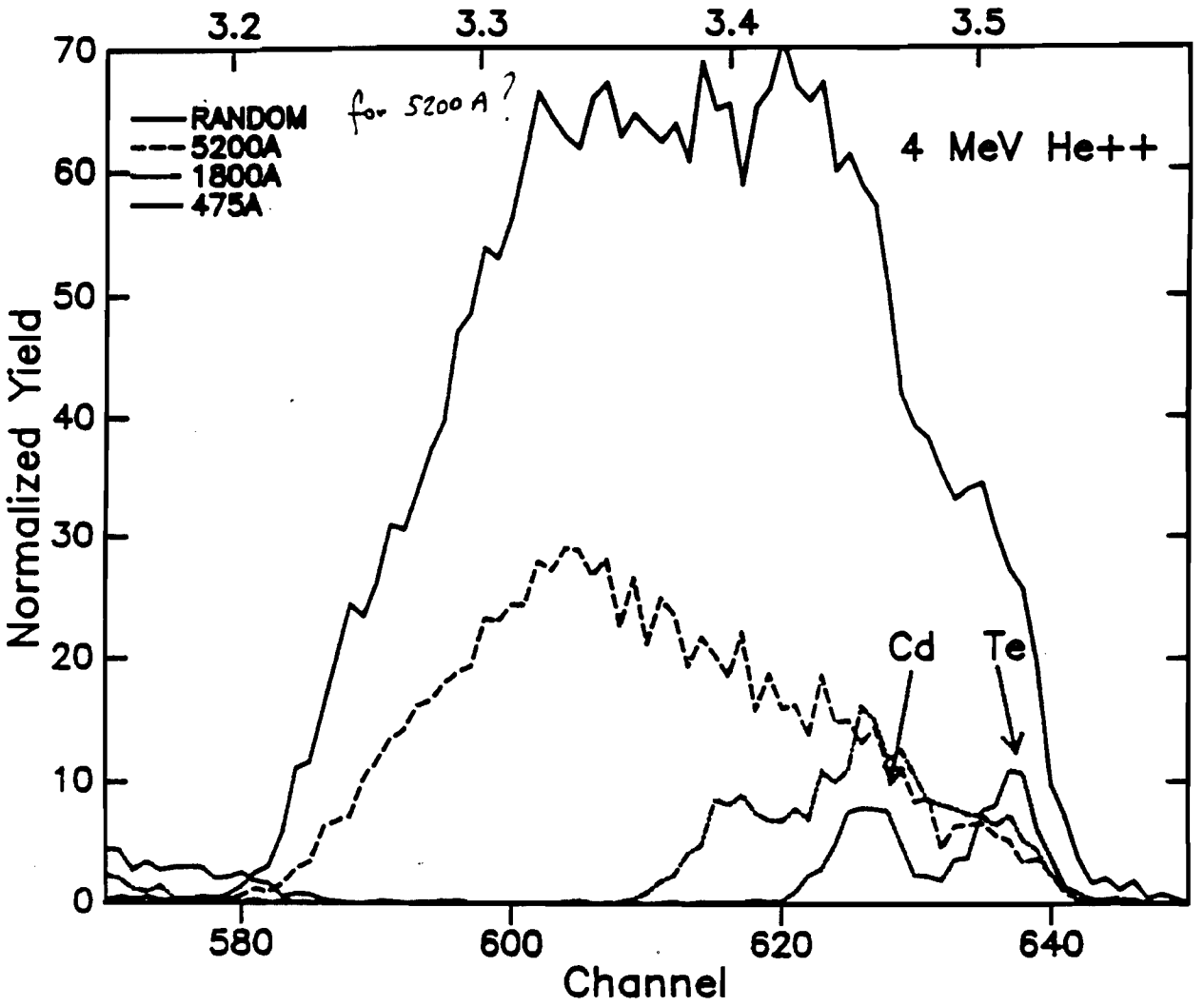
3.2
3.3
3.4
3.5
70
60
50
40
30
20
10
0
RANDOM
5200A
1800A
475A
for 5200 A ?
4 MeV He++
Cd
Te
Normalized Yield
580
600
620
640
Channel

Figure 1

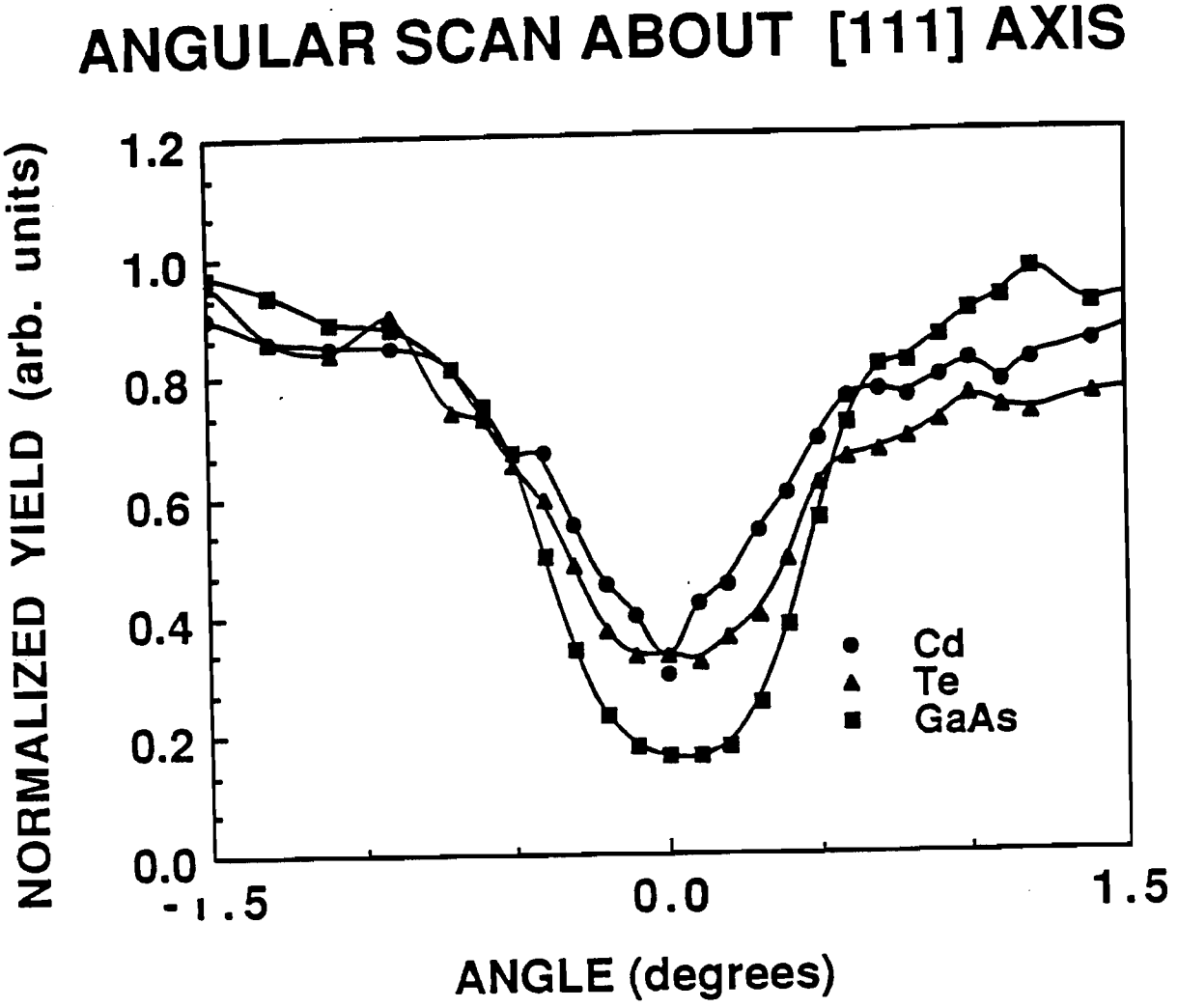
ANGULAR SCAN ABOUT [111] AXIS
NORMALIZED YIELD (arb. units)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-1.5
0.0
1.5
ANGLE (degrees)
Cd
Te
GaAs

Figure 2

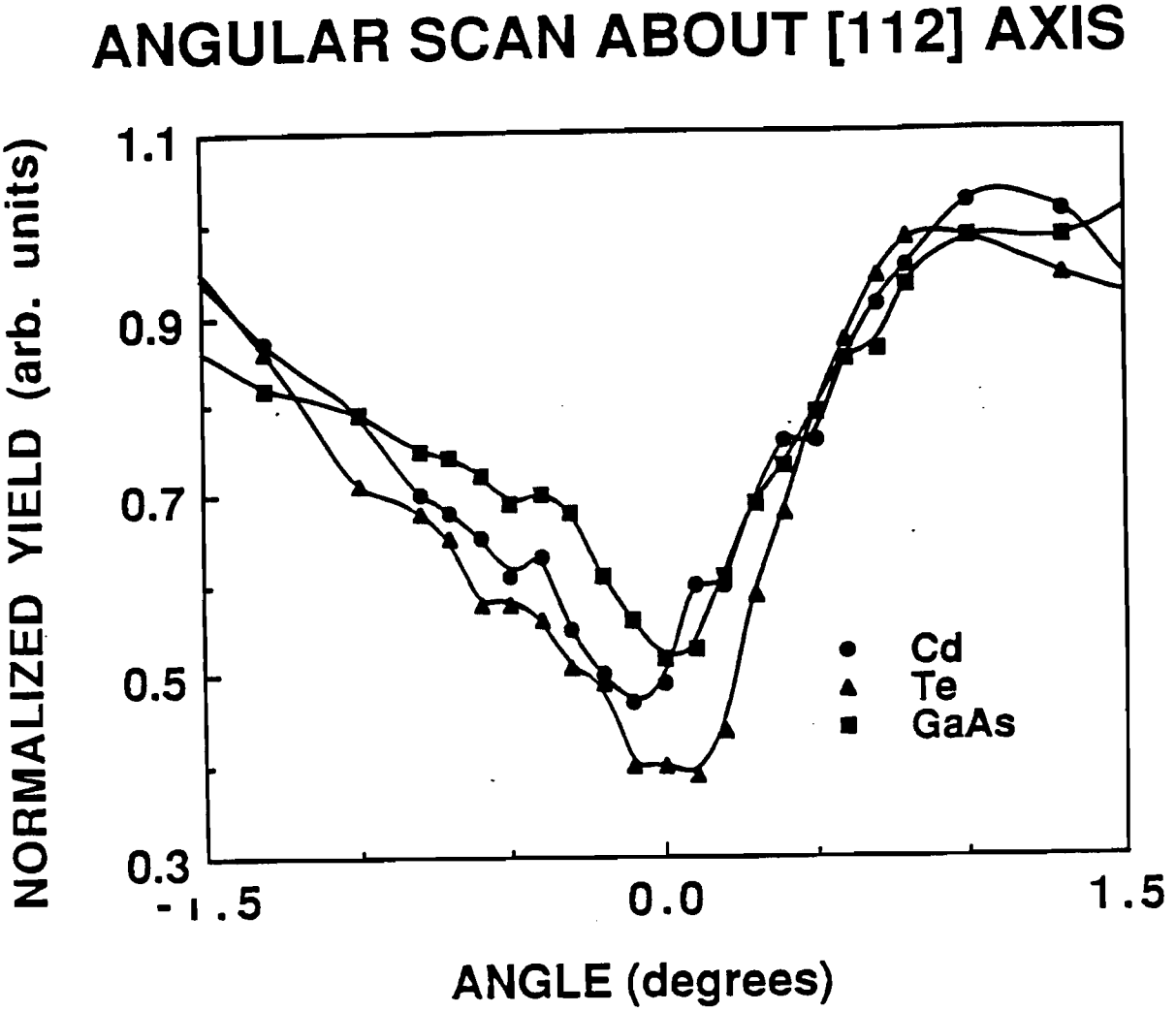
ANGULAR SCAN ABOUT [112] AXIS
NORMALIZED YIELD (arb. units)
1.1
0.9
0.7
0.5
0.3
-1.5
0.0
1.5
ANGLE (degrees)
Cd
Te
GaAs

Figure 3

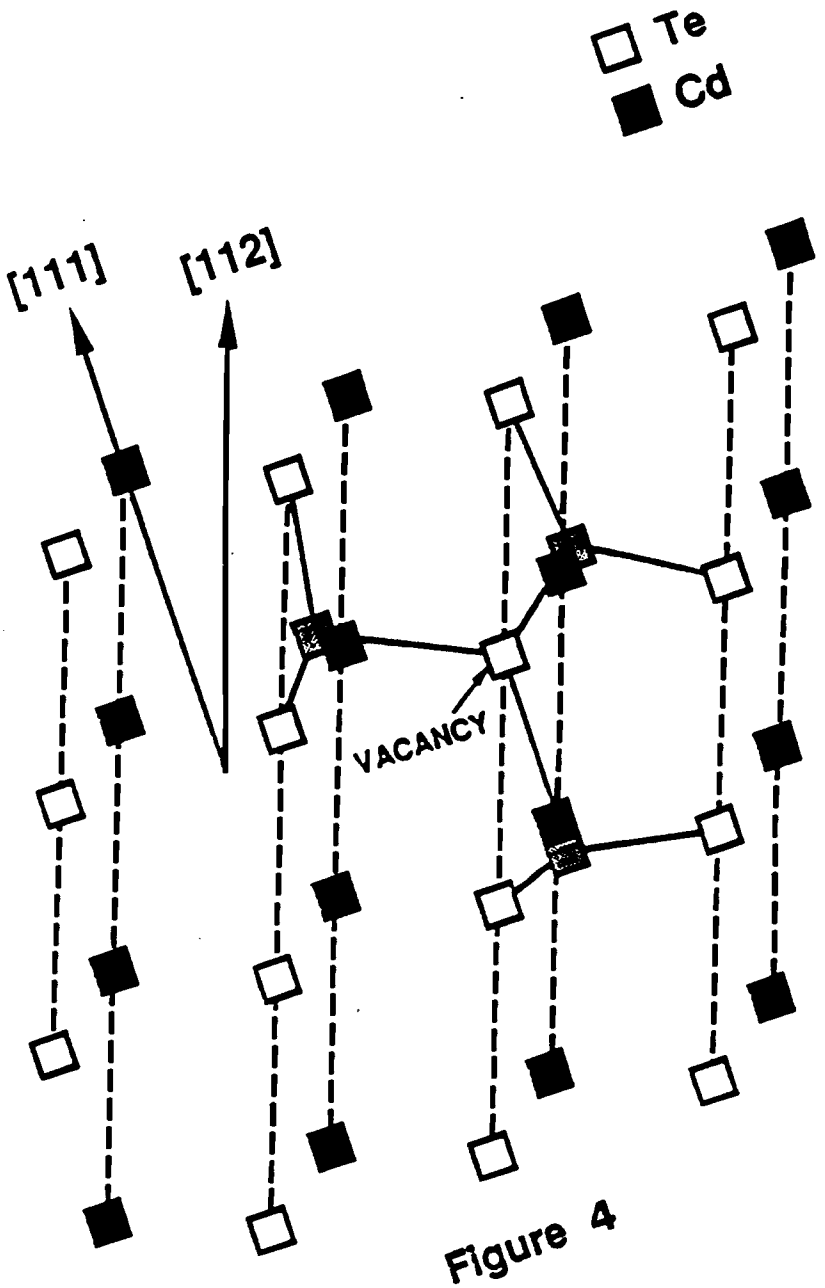

Figure 4

Alfred P. Sloan Research Felloship

Final Report

September 16, 1985 - March 30, 1990

Principal Investigator:

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TABLE OF CONTENTS

STUDY OF HIGH T_c SUPERCONDUCTING THIN FILMS GROWN BY MOCVD

1. Introduction:

In this report, we provide a final summary of the progress made during the grant period (September 16, 1985 - September 16, 1989). Initially the focus of this program was on the development of underlying science and technology for the fabrication of metal-semiconductor superlattices. The major motivation for this work was to search for excitonic superconductivity in these structures as predicted by theory, in addition to the obvious microelectronic applications. After the discovery of superconductivity with transition temperatures above 77K, naturally we have turned our attention also to this new class of materials.

We describe briefly below our work carried under this program on the development of techniques to grow metal-semiconductor superlattices (artificially layered materials) and on the copper oxide based superconductors (naturally layered materials).

2. Study of Artificially Layered Materials

2.1 Thin Film Growth

Currently the major growth technique utilized is the metalorganic chemical vapor deposition (MOCVD) technique. This technique has the capability to grow thin films with atomic level control to fabricate heterostructures and superlattices. The MOCVD technique is also very suitable to the large scale production of electronic and photonic thin films. We have three MOCVD systems operational. The first one is a commercial MOCVD system (Cambridge Instruments, MR102) with 5 MO source lines and 2 hydride lines, suitable for the deposition of a single layer, heterostructure and superlattices. The other two MOCVD systems are homemade and suitable for the

deposition of oxide thin films.

2.2 CVD Precursor Development

The availability of the suitable precursors are essential for successful deposition of the films by the CVD technique. This component of the program focuses on the creation of novel metalorganic compounds suitable for the deposition of rare earth metals, particularly for the deposition of La and LaTe by MOCVD. We have had major breakthroughs in this area in the past three years. I believe that this puts us in a unique position in the world in the deposition of all of the rare earth metals. These precursors will have applications in the metallization of microcircuitry, in the deposition of protective coatings, newly discovered Cu based oxide superconductors and solar cells, etc.

2.3 Study of Non-Oxide Thin Films Grown by MOCVD

In this area, our purpose was to understand the growth conditions and their relationship to the properties of the thin films obtained. Even though the immediate goal was to establish a data base for the growth of LaTe/PbTe superlattices on CdTe buffer layers grown on GaAs, the work has much broader applications in microelectronics and optoelectronics. Among the major achievements in this area are: detailed understanding of the growth mechanism of MOCVD, successful deposition of high quality PbTe films by MOCVD, and first successful deposition of La and LaTe films by MOCVD. The films grown have been characterized for their chemical, structural, electrical and optical properties. The results will be submitted soon for publication in the form of several papers, despite delay due to higher priority given to oxide thin films.

In the study of the MOCVD growth mechanism, we have grown CdTe films on

GaAs (111) wafers systematically to relate the growth rate and the surface morphology to the growth conditions. It is important to understand the growth of CdTe layers, because such layers will be used as the buffer layers for the growth of LaTe/PbTe superlattices. By using a mass transport model through the boundary layer and the gas-solid interface, we have calculated the growth rate as a function of temperature for a broad range, including the mass input limited regime, the diffusion limited regime and the surface kinetic limited regime. We have obtained excellent agreement between the theory and the experiments, as discussed in the preprint attached. On the theoretical side, we have interacted very closely with Prof. Zangwill in the School of Physics at Georgia Tech. Currently, we are extending our understanding of MOCVD from CdTe to growth of other compounds such as PbTe, LaTe and LaTe/PbTe. This work has been carried out in collaboration with P. Anderson of Texas Instruments.

The [111] CdTe/[111] GaAs heterostructure system has been studied in detail by means of MeV ion channeling. It is found that the epitaxy is quite good (backscatter minimum yields of 15%) for thickness greater than 100 Å, which is remarkable considering the 14% lattice mismatch between film and substrate. We have shown that the mismatch results in defects in the interface region in addition to strain produced by epitaxial growth. It has been observed that there is a disturbance in the Cd sublattics as evidenced by displaced Cd atoms protruding into the [211] channels in an asymmetric manner causing an apparent offset in the Cd angular yield minimum. A model was proposed based on Te vacancy density of 1.7% as a possible explanation for the Cd behavior. This work has been in collaboration with B. Wilkens at Bellcore.

We have grown epitaxial layers of PbTe on either GaAs wafers or on CdTe buffer layers grown on GaAs wafers. PbTe grows epitaxially with the [111] direction on GaAs(100) and [100] direction on GaAs(111). Tetraethylead and diisopropyltelluride were used as the MOCVD precursors for low temperature deposition (temperature range 320-450 C). The PbTe films were n- or p-type

depending on the growth conditions. The IR transmission measurements have indicated a sharp absorption at the band-gap energy. We used both Hall effect and IR reflectivity measurements to determine the carrier concentration and mobilities. The mobility for MOCVD grown PbTe films was smaller than the bulk value. This may be a result of microcracks in the film due to thermal expansion mismatch. In support of this idea is the observation of microcracks in most of the PbTe films grown under the optical microscope.

We have deposited La and LaTe thin films in the homemade MOCVD system by using the precursors discovered at Georgia Tech. The suitable deposition temperature range was 550-650 C. These studies were preliminary in nature and were aimed at understanding the decomposition kinetics of the new precursors. Quartz plates were used as substrates. We utilized both argon and hydrogen as the carrier gas. Electron microprobe analysis exhibited up to 10% carbon incorporation in La films grown with Ar carrier gas. We expect great reduction in carbon incorporation in films grown with hydrogen carrier gas. We are in the process of analyzing these films. Also we have observed much less carbon incorporation in LaTe films.

Epitaxial thin films of bismuth telluride, Bi_2Te_3 have been successfully deposited first time on GaAs(111) by MOCVD. Bi_2Te_3 thin films were metallic and can be used to deposit metal-semiconductor superlattices. Also, Bi_2Te_3 is a thermoelectric material and may be used to fabricate monolithic micro-refrigerators to cool semiconductor or superconductor devices. High quality epitaxial films of Bi_2Te_3 were obtained on GaAs(111) substrates at 320^{o}C as evidenced by optical microscopy, x-ray diffraction and ion channeling. Film properties, such as mobility and carrier concentration were studied in the temperature range 80-300K. The films were of p-type with a carrier concentration of 2×10^{20} cm^{-3} at room temperature.

We have utilized various on or off-campus facilities to carry out the characterization of thin films. Double crystal x-ray diffraction experiments

were carried out in collaboration with P. Huang and S. Stock of Materials Engineering, the electron microprobe analysis by G. Freeman of Georgia Tech Research Institute, and IR reflectivity measurements by S. Perkovitz of Emory University. We have also utilized the Hall effect system in A. Rohatgi's laboratory in Electrical Engineering.

We feel that we have acquired large enough data base for the growth of metal-semiconductor superlattices to search for excitonic superconductivity. However, we would like to continue this line of research at a slower pace and concentrate on the artificially layered oxide compounds in the near future, because we can make an immediate impact in this area.

3. Study of Naturally Layered Oxide Superconductors

3.1 Oxide Bulk Material Studies:

Right after the announcement of the breakthrough on the copper-oxide-based high T_c superconductors, we initiated a program on these materials. Even though this effort was initially started by using the funds from a Sloan Research Fellowship and an IBM Faculty Development award, there have been clear overlaps with our DOE contract starting in the summer of 1987.

Our initial work in this area involved the synthesis and characterization of $Y_1Ba_2Cu_3O_7$ compounds in the usual manner. By optimizing the heat treatment and making substitution, we were able to obtain superconductors on a routine basis with transition temperatures above 90 K. Starting in July of 1987, our focus shifted to the discovery of superconductivity at even higher temperatures. After a careful systematic study, we were led to several compositions exhibiting evidence of possible superconductivity at room temperature or above. The highest observed onset temperature is 550 K. This work is described in detail in a paper submitted to Physical Review B. The fraction of the superconducting phase seems to be very small (1 part in 10^4).

3.2 Oxide Thin Film Studies:

Our research effort in this area in the past two years has focused on the development of the MOCVD technique to provide high quality superconducting thin films on large area substrates for fundamental studies and device applications. We have successfully deposited thin films of $Y_1Ba_2Cu_3O_{7-x}$ and $Tl_2CaBa_2Cu_2O_y$ by MOCVD with high quality. The results have been reported in the form of several papers and invited talks. The papers are provided in the attachment. Our results show that after post annealing, C-axis oriented $YBa_2Cu_3O_{7-x}$ superconducting films can be obtained reproducably with a transition onset temperature at 93K and a zero-resistance temperature at 84K on yttria-stabilized zirconia (100) (YSZ) substrates. Superconducting $Tl_2CaBa_2Cu_2O_y$ thin films have been grown on single crystal sapphire $(1\bar{1}02)$ substrate without a buffer layer. Superconducting transition temperatures with onset above 100K and zero-resistance at 94K has been obtained with heat treatment at 500°C in oxygen.

The use of superconducting coatings and thin films is severaly limited at this point because of the lack of suitable substrates. The most widely used substrates are MgO(100), YSZ and $SrTiO_3$. However, these substrates are very expensive and not available with large areas. To address this problem we have started depositing these materials by MOCVD on common substrates, such as glass plates, silicon and sapphire. The MgO film deposited on a glass plate had very smooth surface morphology and was optical quality. It had also almost one hundred percent texturing with (100) direction perpendicular to the substrate surface. The detailed results are provided in a paper provided in the attachment. This is surprising in view of the fact that glass substrate is amorphous and MgO has a cubic structure. Next we would like to deposit superconducting thin films on these (100) oriented MgO buffer layers deposited on glass plates. It is well known that single crystal MgO (100) substrates

give high quality superconducting films with very high critical currents (T_c ~ 10^6 A/cm^2). Therefore the growth of oriented MgO films on common cheap substrates as buffer layers may have profound implications for the large scale utilization of the superconducting thin films and coatings.

4. Publications Under This Grant

1. "Evidence for Possible Stable Superconductivity at 500K", A. Erbil, A. C. Wright and E. P. Boyd, Phys. Rev. B37, 555 (1988).

2. "Metalorganic Chemical Vapor Deposition of Highly Textured Superconducting $YBa_2Cu_3O_{7-x}$ Films", K. Zhang, B. S. Kwak, E. P. Boyd, A. C. Wright and A. Erbil, in "Science and Technology of Thin Film Superconductors", ed. by R. D. McConnell and S. A. Wolf (Plenum, New York, 1989), p. 271.

3. "C-Axis Oriented $YBa_2Cu_3O_{7-x}$ Superconducting Films by Metalorganic Chemical Vapor Deposition", K. Zhang, B. S. Kwak, E. P. Boyd, A. C. Wright and A. Erbil, Appl. Phys. Lett. 54, 380 (1989).

4. "Metalorganic Chemical Vapor Deposition of [100] Textured MgO Thin Films", B. S. Kwak, E. P. Boyd, K. Zhang, A. Erbil, and B. Wilkens, Appl. Phys. Lett. 54, 2542 (1989).

5. "Metalorganic Chemical Vapor Deposition of $Tl_2CaBa_2Cu_2O_y$ Superconducting Thin Films on Sapphire", K. Zhang, E. P. Boyd, B. S. Kwak, A. C. Wright, and A. Erbil, Appl. Phys. Lett. 55, 1258 (1989).

Accepted for Publication

1. "MeV Ion Channeling Studies of [111] CdTe Films on [111] GaAs Substrates", B. Wilkens, K. Pollard and A. Erbil (J. Appl. Phys.).

In Preparation

1. "Growth Mechanism of CdTe Films by Organometallic Vapor Phase Epitaxy", A. Erbil and P. L. Anderson (for Appl. Phys. Lett.).

2. "OMVPE Growth and Properties of PbTe Films on GaAs", A. Erbil and K. T. Pollard (for Appl. Phys. Lett.).

3. "Organometallic Vapor Phase Epitaxy of Bi_2Te_3 on GaAs (111)", A. Erbil, K. T. Pollard and B. Wilkens (for J. Electronic Mat.).

5. Meetings and Symposia Under This Grant

A) Invited

1. A. Erbil, "Possible Very High T_c Superconductors", Panel discussion, Materials Research Society Meeting, April 5-8, 1988, Reno, Nevada.

2. A. Erbil, K. Zhang, B. S. Kwak, E. P. Boyd and A. C. Wright, "C-Axis Oriented $YBa_2Cu_3O_{7-x}$ Superconducting Films by Metalorganic Chemical Vapor Deposition", Conference on the Science and Technology of Thin Film Superconductors, November 14-18, 1988, Colorado Springs, Colorado.

3. A. Erbil, K. Zhang, B. S. Kwak and E. P. Boyd, "A Review of Metalorganic Chemical Vapor Deposition of High-Temperature Superconducting Thin Films", SPIE's 1989 Symposium, Oct. 8-13, 1989, Santa Clara, CA.

B) Contributed

1. A. Erbil and P. L. Anderson, "MOCVD Growth Mechanisms of II-VI Compounds", Bull. Am. Phys. Soc. 32, 530 (1987).

2. P. L. Anderson and A. Erbil, "MOCVD of II-VI Compounds", Epicon '87, November 16-20, 1987, South Africa.

3. A. Erbil, A. C. Wright and E. P. Boyd, "Evidence for Possible Stable Superconductivcity at 500 K", Symp. High T_c Superconductors, Materials Research Society, Nov. 30-Dec. 3 (1987), Boston, MA.

4. A. Erbil and K. T. Pollard, "Study of MOCVD Grown PbTe Films", Bull. Am. Phys. Soc. 33, 246 (1988).

5. B. Wilkens and A. Erbil, "Ion Channeling Studies of the MOCVD Grown CdTe Films on GaAs", Materials Research Society Meeting, Boston, MA, Nov. 28 - Dec. 3, 1988.

6. A. Erbil, K. Zhang, B. S. Kwak, E. P. Boyd and A. C. Wright, "C-Axis Oriented $YBa_2Cu_3O_{7-x}$ Superconducting Films by Metalorganic Chemical Vapor Deposition", Conference on the Science and Technology of Thin Film Superconductors, November 14-18, 1988, Colorado Springs, Colorado.

7. K. Zhang, B. S. Kwak, E. P. Boyd, A. C. Wright, and A. Erbil, "Effects of Substrate and Post-Annealing Conditions on Metalorganic Chemical Vapor Deposition of $YBa_2Cu_3O_{7-x}$ Thin Films", Bull. Am. Phys. Soc. 34, 603 (1989).

8. A. Erbil, K. Pollard and B. Wilkens, "Study of Bi_2Te_3 Thin Films Grown by MOCVD", Bull. Am. Phys. Soc. 34, 937 (1989).

9. B. S. Kwak, E. P. Boyd, K. Zhang, and A. Erbil, "Growth of Highly Textured MgO Thin Films by MOCVD", Bull. Am. Phys. Soc. 34, 937 (1989).